United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S7-82-048 Sept. 1982

EPA

Project Summary

Laboratory Evaluation of Level 1 Organic Analysis Procedures

Judith C. Harris, Zoe A. Grosser, Philip L. Levins, Debra J. Sorlin, and Clifford H. Summers

Level 1 is the first stage in a three-tiered approach to performing an environmental source assessment. Level 1 is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. A set of sampling and analysis procedures designed to achieve these objectives was developed and published in EPA report EPA-600/2-76-160a in June 1976. That methodology was based on previously available laboratory procedures, which had not, however, been specifically tested to determine their suitability for this particular purpose. The overall objective of the work described in this report was to evaluate the Level 1 *organic* sampling and analysis procedures as proposed in the June 1976 manual. Priorities of this study included: development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures, and identification of problems and limitations of the proposed procedures that might require revisions in methodology. This report gives results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. The report also includes several examples of Level 1 organic analysis data for samples analyzed according to the revised procedures. The results for coal, fuel oil, and SASS train samples of an actual emission source are presented in the Level 1 report format.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

EPA/IERL-RTP's Technical Support Staff has developed a three-tiered or phased approach to performing an environmental source assessment. The first phase, Level 1, is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. The Level 1 assessment is intended to: 1) provide preliminary environmental assessment data, 2) identify principal problem areas, and 3) provide the data needed for prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials, for further consideration in the overall assessment. The second phase of sampling and analysis, Level 2, is designed to provide additional information that will confirm and expand the information gathered in Level 1. The third phase, Level 3, will permit quanti-

tative monitoring of specific pollutants identified in Level 2.

A set of sampling and analysis procedures designed to achieve the objectives of Level 1 environmental assessment was developed and published in an EPA report in June 1976.[1] The Level 1 procedures are comprehensive, covering inorganic and organic chemical analysis, and biological testing. The overall objective of the work described in this report was to evaluate the Level 1 *organic* sampling and analysis procedures as proposed in the June 1976 manual. This methodology was designed to identify the major classes of organic compounds present in a process or effluent stream and to estimate their concentrations. Priorities of this study included: development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures, and identification of problems and limitations of the proposed procedures that might require revision in methodology.

The report gives results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. The report also includes several examples of Level 1 organic analysis data for samples analyzed according to the revised procedures. The results for coal, fuel oil, and SASS train samples of an actual emission source are presented in the full Level 1 format in the complete report; selected examples are included in this summary.

An integrated overview of the evaluated and revised procedures are in Chapter 9 of the second edition (October 1978) of the Level 1 procedures manual.[2] The Level 1 organic analysis methodology includes procedures for sample preparation, an open-column liquid chromatographic (LC) procedure to separate the extract into fractions prior to analysis, quantitative analysis of total organic content by gas chromatography (TCO) and gravimetry (GRAV), and qualitative analysis of compound types by infrared (IR) and low resolution mass spectrometry (LRMS).

Summary of Experimental Studies

The following paragraphs briefly summarize each experimental study performed in this work.

Field GC Analysis of Organic Gases

The original Level 1 procedures[1] recommended that organic gases (species with boiling points $<100°C$) be collected in glass sampling bulbs and analyzed on-site by gas chromatography (Field GC procedure). Although the possibility of substituting polymeric plastic sampling bags was advocated, systematic studies[3] indicated that glass bulbs were the sampling system of choice for Level 1. Time-integrated sampling of gases with evacuated glass bulbs can be achieved if a glass fiber filter and a 0.2 Lpm critical flow orifice are used upstream of the bulb. The original GC procedures for gas chromatographic analysis of sulfur gases and gaseous hydrocarbons were reviewed and found to be unsatisfactory for Level 1. Revised procedures using alternative columns and GC temperature programs were tested and recommended as replacements.

Preparation and Characterization of XAD-2 Resin

A macroreticular crosslinked polystyrene resin, XAD-2, was selected for the SASS train organic vapor sampling module because of its high collection efficiency for a variety of organic compounds. The optimum procedures for preparation (cleanup) and analysis of the blank for XAD-2 resin were not specified in the June 1976 manual[1]. Two different resin preparation procedures (water + methanol + pentane and water + methanol + methylene chloride) were compared to the original 4-step procedure (water + methanol + diethyl ether + pentane). Parameters investigated include the surface properties of resin (pore volume and pore size distribution) and the quantity and nature of residual solvent extractable material. Further experiments examined the possibility of resin self-contamination by thermal processes (at 20°, 40°, and 60°C) and the efficiency of recovery of spiked materials. Based on these studies, the new recommended procedure is to clean the XAD-2 resin with the water+ methanol+ methylene chloride overnight extraction sequence and to extract the collected SASS sample with methylene chloride.

Extraction of Aqueous Samples

The June 1976 manual[1] suggested that aqueous samples be adjusted to neutral pH and then sequentially extracted with three 500-mL portions of methylene chloride for a 10-L water sample. A literature study of the efficiency to be expected from methylene chloride solvent extraction of aqueous samples indicated that the original Level 1 procedure[1], which called for three extractions at neutral pH, was inadequate for Level 1, since moderately strong organic acids and bases would be $<0.1\%$ extracted. A revised procedure for Level 1 extractions at both acidic and basic pH was proposed and evaluated. Neutral species, whose recovery is independent of pH, are essentially extracted four times by this procedure; acidic and basic species are each extracted twice. It had been suggested that ether may be superior to methylene chloride for extracting certain acidic compounds, such as phenols or carboxylic acids. This was tested experimentally to see if the advantage was significant. Four of the five model compounds tested were extracted efficiently with either methylene chloride or ether. One compound, phenol, was extracted four times more efficiently by ether than by methylene chloride (yielding an 82% recovery versus only 20%), although higher homologs of phenol (such as cresols) are adequately extractable with methylene chloride. The improvement in efficiency for a few specific compounds did not appear to warrant a change to the less convenient (lighter than water) solvent; methylene chloride remained the recommended Level 1 solvent.

Extraction of Sludge/Slurry Samples

The June 1976 manual[1] included no explicit Level 1 procedures for preparation of sludge/slurry samples prior to organic analysis. This sample category can span a broad range, including slurries and solids or semisolid sludges containing 95% water. Some of these materials are very difficult to handle and no one procedure will work for all of them. Nevertheless, it was desirable to define a sample preparation protocol that could be applied consistently and that would minimize variability. A protocol was tested using a variety of complex sludge/slurry samples. It involves, in most cases, tests on small portions of the sample to determine the best procedure prior to committing the entire sample. The basic approach is to determine whether the sample is best

treated as a solid, as a liquid, or by a combination of procedures.

Analyses of Volatile Species in Organic Extracts: TCO and Solvent Exchange

The original Level 1 organic analysis procedure, specified in the June 1976 manual[1], was designed to provide qualitative compound class identification and quantitative (gravimetric) data for components of a sample that are retained when an organic sample extract is evaporated to dryness. In the experimental investigation of the LC-IR-LRMS organic analysis procedure, it became apparent that the range of material lost when the sample extract was evaporated to dryness for the gravimetric analysis and preparation of the LC sample was considerably higher than expected. Quantitative retention of the model compounds appeared to be achievable only for species with boiling points of about 300°C and above. At about the same time, it was recognized that many, if not most, of the organic compounds that were considered to be of primary concern in environmental assessment [e.g., the compounds on the Multimedia Environmental Goals (MEG) list[4]], were in the <300°C boiling point range. Preliminary studies indicated that the dramatic loss of moderately volatile material occurs only after the sample has been evaporated to dryness; concentration of an extract by a factor of 10 to 100 (1 or 0.1 mL final volume from 10 mL extract) produces less drastic losses.

It was decided to modify the procedures for preparation of sample extracts to include a solvent exchange step prior to LC. This avoids evaporating the sample to dryness and thus allows acquisition of qualitative chemical information about species in the <300°C boiling point range. It was also necessary to specify an alternative procedure for quantitative analysis of materials in the 100-300°C range; a procedure based on gas chromatography with a flame ionization detector (FID) was investigated. A satisfactory column for this Total Chromatographable Organics (TCO) was found to be 1.8 m x 3 mm (6 ft x ⅛-in.) O.D. 10% OV-101 on 100/120 mesh Supelcoport. The GC was operated isothermally at about 30°C — or room temperature — for 5 minutes after sample injection and then programmed rapidly to 250°C and held as long as necessary. From a calibration curve based on n-hydrocarbons and the total integrated area of a GC trace, the TCO of the example environmental sample extract is estimated.

Elution Patterns in Level 1 LC

Several sets of mixtures of pure compounds were prepared to evaluate the elution patterns of the Level 1 LC separation.[1] The mixtures were generally applied to the columns at levels corresponding to <25 mg of each compound to avoid overloading the column and therefore distorting the separation.

A table, showing results of LC elution pattern studies of 17 model compounds, is given in the full report. The data illustrate a phenomenon borne out in subsequent work: it is uncommon to find any given material isolated in one LC fraction. Several years of cumulative experience with the Level 1 LC separation have led to the inference that the band-broadening in this low resolution chromatographic method leads to elution peaks that are about 1 LC fraction wide.

There was concern that the presence of water in Level 1 organic extracts might lead to irreproducible deactivation of the silica gel and, therefore, to irreproducible results of the LC separation. Experimental results indicated that sodium sulfate may be used as a dryer for methylene chloride extracts without causing unacceptable losses of sample components.

It was also suspected that the most polar solvents used in the LC scheme might dissolve some of the silica gel from the column bed, giving rise to spurious high values in the gravimetric analysis. The data were obtained for blank columns with no sample added indicating that 0.9 ±0.2 mg of silica gel was found in the eluant of Fraction 7; no weighable material was found in Fractions 1 through 6. It appeared to be necessary to correct the apparent weights of Fraction 7 arithmetically, by subtracting the appropriate blank value, rather than by actually separating the sample from the silica gel.

Ruggedness Testing of Level 1 LC Procedure

It was desirable to determine the change in results of the LC separation that might occur if a slight deviation in procedure was made. This margin of error within which an experiment can be varied without changing the results is commonly referred to as the "ruggedness" of the experiment. If the procedure can be done slightly differently each time and the same results obtained, chances are increased that intralaboratory or even interlaboratory results will be consistent and comparable.

The Level 1 LC procedure was studied for ruggedness in three aspects: continuity of elution, exact composition of eluants, and activity of silica gel.

In all cases a solution of model compounds with a convenient elution pattern was used to test the procedures. The fractions were analyzed by GC (using the Level 1 TCO program) and compared to controls. No significant change in the elution pattern, compared to the control LC procedure, was observed under any of the following conditions: 0.5-hr interruption in LC elution; use of month-old vs fresh elution solvents; activation of silica gel at times (2-24 hrs) and temperatures (90-200°C) other than those specified in the procedure; and LC column temperature varied from 14.5 to 22°C.

Report Formats for Level 1 Organic Analysis Results

A particularly important aspect of the evaluation and evolution of the Level 1 organic analysis procedures was the development of systematic reporting formats that summarize and integrate the data usefully. The report formats developed in this study are incorporated in the October 1978 manual.[2] They are described briefly in this summary; complete examples are given in the full report.

In interpreting and integrating the Level 1 organic analysis data and reporting the results, a list of organic compound categories, based on the Multimedia Environmental Goals (MEG)[4] categorization scheme (slightly modified), was used to organize the Level 1 data. It should be emphasized that it is the list of MEG *categories,* and not the list of specific MEG compounds, that is referred to in the context of Level 1 organic analysis. With the addition of a very few non-MEG compound classes, this list of categories represents almost all of the organic chemistry likely to be encountered in most sources. In developing this report format for Level 1 organic analysis results, it was assumed that users of Level 1 EA data would be interested in comparing estimated mass loadings in various streams with decision criteria expressed as concentrations. A

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requirement of the approach is that all data reduction steps described in this document be performed by personnel with access to the original Level 1 organic analysis data and/or direct communication with the original analyst(s). The reason for this is that the organic analysis data outputs (e.g., spectra) contain much information (e.g., presence or absence of particular peaks) that is not easily reduced to tables or other forms intelligible to nonchemists, but is very valuable in assessing the Level 1 sampling and analysis results.

Results of the LC fractionation procedure include quantitative estimates of TCO and GRAV range materials in each of seven fractions. GRAV analyses involve weighing to the nearest 0.1 mg. TCO values and all Level 1 concentration data are reported to 1 or 2 significant figures.

The total sample extract, or neat organic liquid, and the seven LC fractions are analyzed by IR spectroscopy. Spectra are interpreted in terms of the functional group types present in the major components of the sample or LC fraction. Interpretation of the spectrum is guided by consideration of the LC fractionation scheme and the LRMS results. Components amounting to <5% of the total sample will not contribute significantly to the IR spectrum and cannot be detected by this technique.

The report format for the results of the IR analysis includes specification of frequencies, intensities, and assignments for all major peaks in the spectrum.

LRMS are obtained on each LC fraction which has sufficient quantity to potentially exceed decision criteria levels of organic pollutants. Samples with significant quantities of TCO range material are analyzed by insertion in the batch inlet; all samples require analysis by direct insertion probe.

At the end of the Level 1 organic analysis procedure, there will be an LC report, eight IR reports, and up to seven LRMS reports for each organic extract or neat organic sample. This is an unwieldy body of data from which to make a decision. These data are reduced to a workable form by preparing a single table that summarizes the organic analysis results for each extract.

References

(1) Hamersma, J.W., S.L. Reynolds, and R.F. Maddalone, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," EPA-600/2-76-160a, NTIS No. PB 257-850, June 1976.

(2) Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201, NTIS No. PB 293-795, October 1978.

(3) Thrun, K.E., J.C. Harris, and K. Beltis, "Gas Sample Storage," EPA-600/7-79-095, NTIS No. PB 298-350, April 1979.

(4) Cleland, J.G. and G.L. Kingsbury, "Multimedia Environmental Goals for Environmental Assessment, Volume I," EPA-600/7-77-136a, NTIS No. PB 276-919, November 1977.

Judith C. Harris, Zoe A. Grosser, Philip L. Levins, Debra J. Sorlin, and Clifford H. Summers are with Arthur D. Little, Inc., Cambridge, MA 02140.

***Larry D. Johnson** is the EPA Project Officer (see below).*

The complete report, entitled "Laboratory Evaluation of Level 1 Organic Analysis Procedures," (Order No. PB 82-239 294; Cost: $18.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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