ORGANIC ANALYSIS FOR ENVIRONMENTAL ASSESSMENT

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September 1977

Abstract

A survey analysis approach for organic materials is presented. The scheme presented is relatively simple and inexpensive, yet produces useful information which can be utilized to decide whether more sophisticated and expensive methods are justified. A selection of Level 1 data from environmental samples is presented.

A brief discussion of Level 2 analysis techniques is also included.

INTRODUCTION

Two of the major responsibilities of EPA's Industrial Environmental Research Laboratory in North Carolina (IERL/RTP) are control technology development and environmental assessment. Due to a growing awareness and concern over the effect of pollution in our surroundings, the current emphasis is on environmental assessment.

Worldwide energy shortages have added momentum to development programs for alternate or modified energy or fuels production. It is particularly important that these emerging technologies be evaluated, as they develop, for their potential environmental insult. By means of such early investigation, problem processes may be modified at the most effective and economical stage, or control technology may be developed in parallel with production technology.

Only a few existing industrial processes have been reasonably well characterized with respect to their release of a few selected pollutants. Far fewer, if indeed any, processes have been adequately studied for a wide range of potentially harmful materials. For this reason, control technology needs will remain undefined until the potential environmental effects are estimated.

Environmental assessment is a formidable task, technically difficult, and extremely expensive. In order to help maximize the information gain of such programs and to minimize the costs, special approaches have been developed to sampling and analysis programs for environmental assessment. This paper discusses one part of such an approach: organic analysis employed in Level 1 of an environmental assessment.

FUNDAMENTALS

Before discussing the organic analysis approach employed in Level 1 of an environmental assessment, it is appropriate to consider some of the pertinent terminology. To say that an environmental assessment is a project involving problem definition with regard to pollutant source environmental insult is convenient, but perhaps an oversimplification. A longer, but more complete, description is that an IERL/RTP environmental assessment contains: (1) a systematic evaluation of the physical, chemical, and biological characteristics of all streams associated with a process; (2) predictions of the probable effects of those streams on the environment; (3) prioritization of those streams relative to their individual hazard potential; and (4) identification of any necessary control technology programs.

Examination of several strategies for environmental assessment sampling and analysis led to the conclusion that a phased approach was the most cost and information effective. The phased approach has been discussed in several recent publications (1, 2, 3, 4). This strategy makes use of three levels of sampling and analysis: Level 1 is a survey phase; Level 2 is a directed detailed analysis, based on Level 1 information; and Level 3 involves monitoring of priority pollutants selected by use of information generated during the two previous phases. Level 1 sampling and sample preparation procedures are dealt with in several publications (5, 6, 7, 8). A flow chart of the Level 1 analysis scheme, shown in Figure 1, contains four major divisions of analysis: physical, inorganic chemical, organic chemical, and biological. Organic analysis will be the primary topic discussed from this point on.

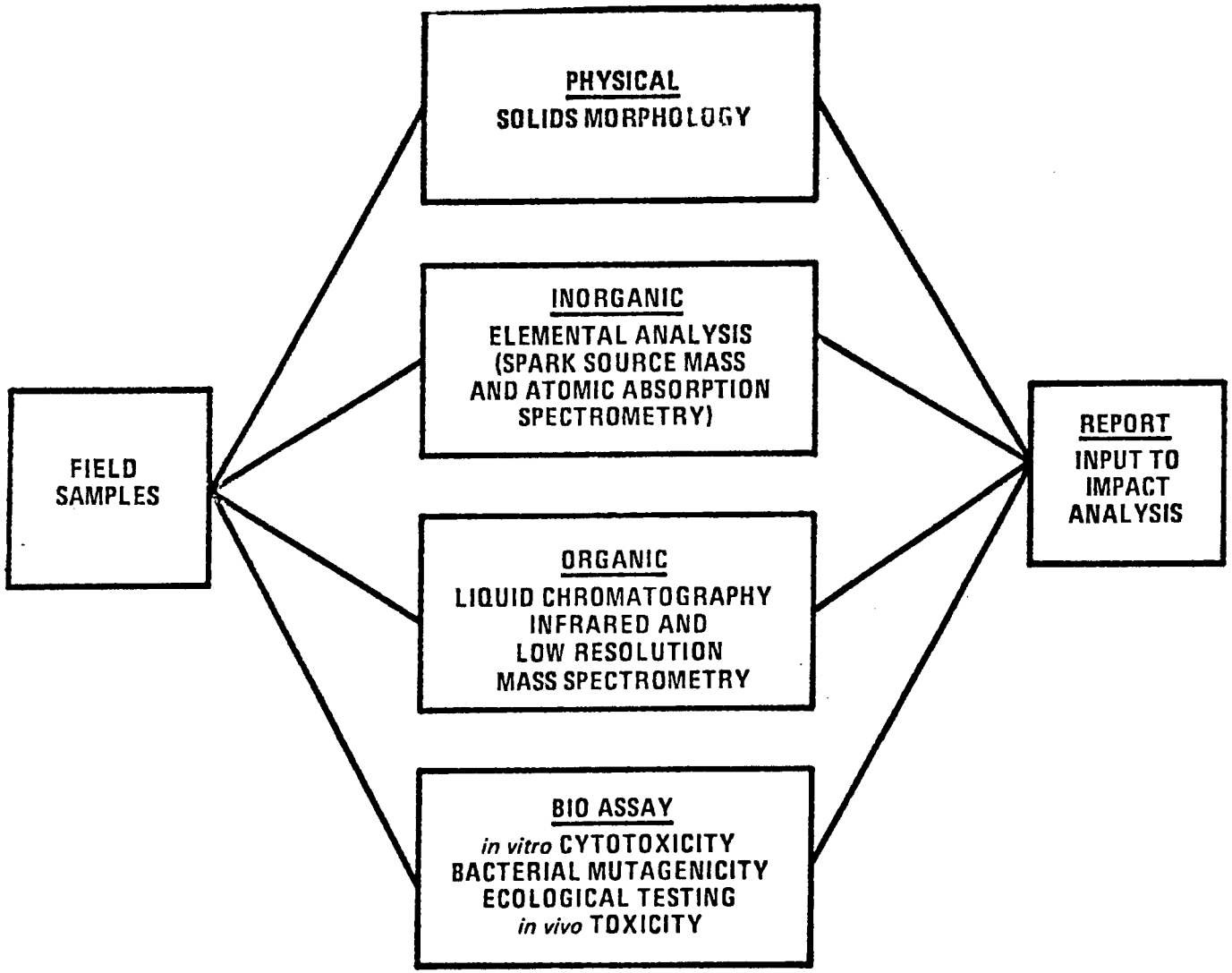

Figure 1. Flow chart of level 1 scheme.

ORGANIC ANALYSIS OVERVIEW

Current analytical technology makes it possible to identify and quantify virtually all of the organic constituents of even the most complex mixture, given sufficient sample, funds, and time. Obviously all three will not be available for every case; hence, adjustments must be made in the degree of information expected from the sample. Specific compound identification should not, in general, be expected at costs commensurate with the Level 1 philosophy. Therefore, the scheme presented is relatively simple and inexpensive, yet produces information which can be utilized to decide whether more sophisticated and expensive methods are justified. The Level 1 organic analysis produces data in terms of chromatographic classes of compounds and characteristic infrared absorption bands. The Level 1 organic analysis strategy shown in Figure 2 shows four analytical operations that are central to the scheme.

Liquid chromatographic separation (Appendix A.1) is the heart of the whole approach. It is an analytical step (in that behavior of a given class of compounds is predictable) as well as a separation step (since the fractions may be further analyzed much more readily than the original mixture). The behavior of selected classes of compounds with respect to the chromatographic analysis is shown in Figure 3. Distribution of a few selected compounds is shown in Figure 4.

The second analysis operation is determination of total organics content. This operation allows quantitation of the organics in each of the chromatographic fractions as well as aliquot size selection for optimum column operation. The original Level 1 scheme (8), as well as the first revision (5), depended entirely upon reduction to dryness and weighing for total organics determination. Recent data show that many materials in the boiling range below 275°C may be partially lost by that approach (9). Accordingly, a gas chromatography procedure for volatile organics has been adopted as a part of the Level 1 strategy (Appendix A.2). Total organic content is obtained by addition of the gravimetric results and the total chromatographable organics (TCO).

The third analysis operation is infrared absorption spectrophotometry. This classical technique is often overlooked in today's mass-spectrometry-dominated laboratory, but still remains a powerful tool which provides considerable information at moderate cost. Infrared spectra of the eight chromatographic fractions may be used to confirm the absence or presence of particular compound classes or functional groups as indicated by the chromatograhic data. It is occasionally possible to obtain specific compound identification from the infrared spectra; but as previously mentioned, the complexity of most environmental samples makes this the exception rather than the rule.

The fourth analytical operation of the Level 1 organic scheme is low resolution mass spectrometry (LMRS). This particular tool, sitting firmly in the middle of the transition zone between Level's 1 and 2, causes many philosophical problems concerning its proper utilization. The original Level 1 scheme did not contain LRMS (8); but, it was included in the modified strategy (5) to prevent potential triggering of Level 2 efforts based on large amounts of suspicious, but innocuous, organics. LRMS can be a very powerful tool, especially when combined with the other Level 1 components. In many cases, compound identification and quantification are possible when the entire scheme is applied. What, then, are the philosophical problems?

The first and foremost problem is cost. One LRMS application including interpretation costs about $100, not a large sum compared to overall Level 1 costs. If LRMS is necessary on only one or two fractions, then costs are nominal, information gain is considerable, and cost effectiveness is high. In the worst case, however, one may be forced to apply LRMS to all eight fractions and employ both probe and batch modes of sample introduction. The resultant LRMS cost is $1600 per sample, a significant increase. The cost impact of such a per-sample increase may be forcefully illustrated by the following hypothetical example.

If three flue gas samples are taken with a Source Assessment Sampling System (SASS) at each of 50 plants, the resulting number of subsamples requiring Level 1 organic analysis

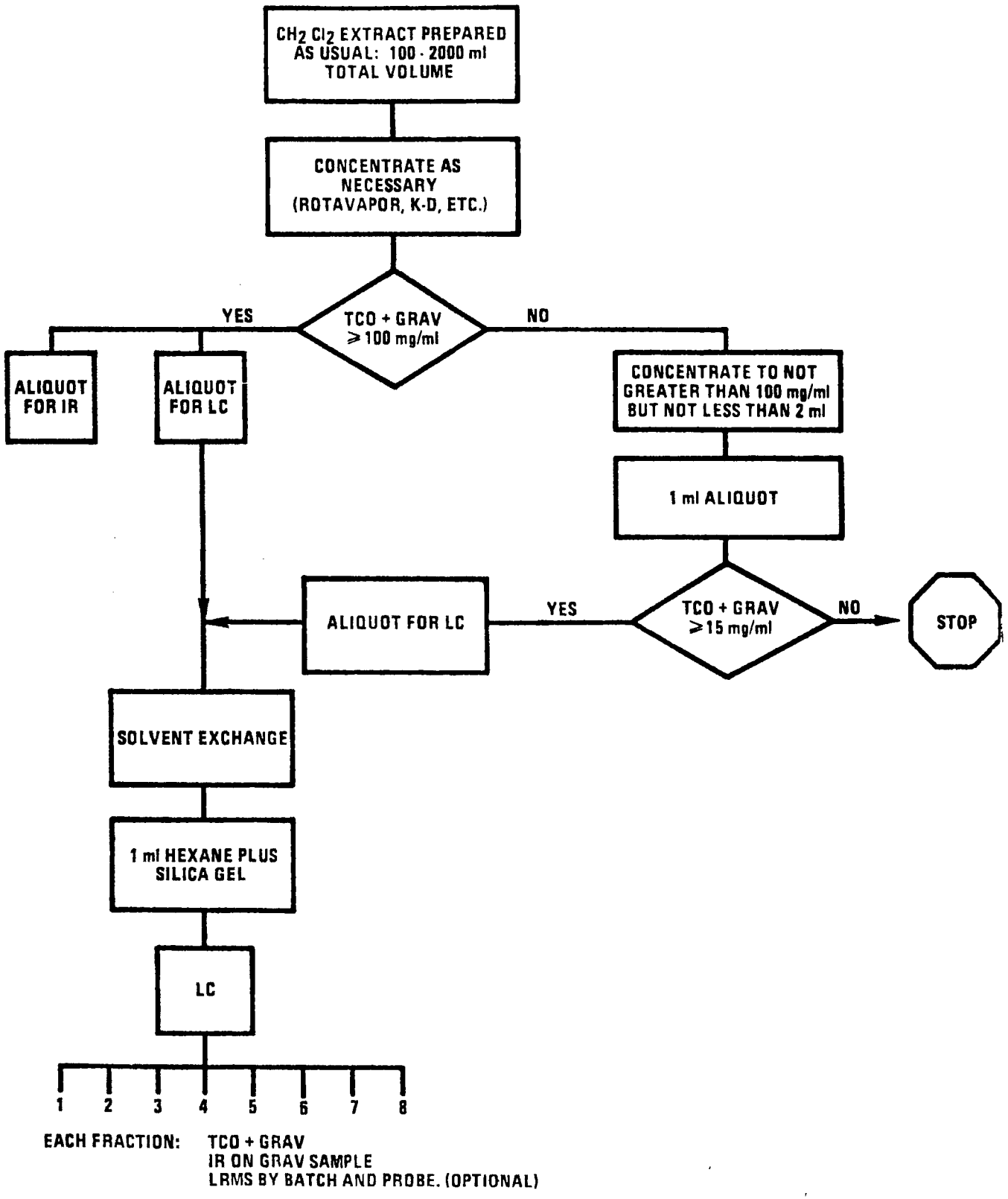

Figure 2. Modified level 1 organic analysis procedure.

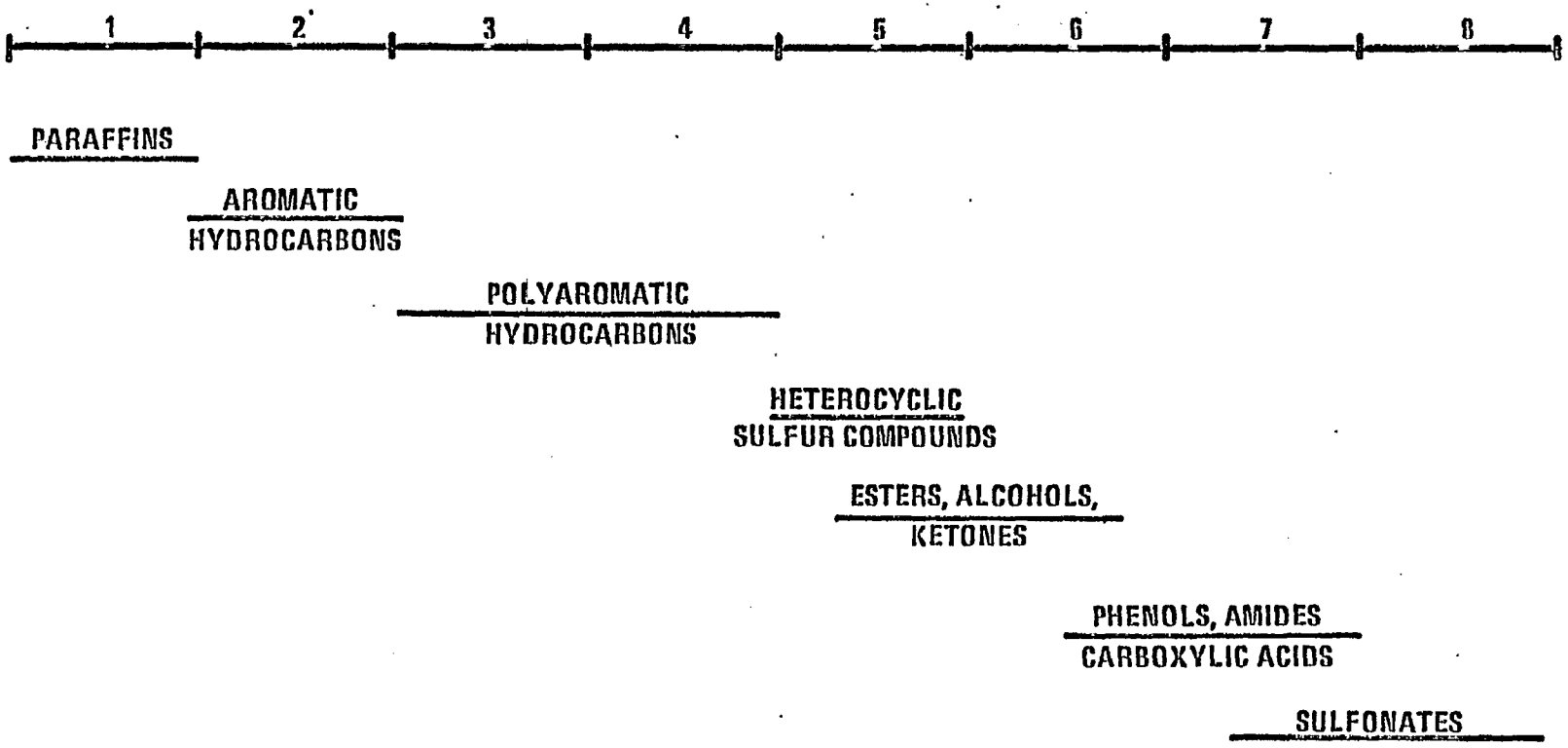

Figure 3. Liquid chromatographic fractions v. class types.

COMPOUND	1	2	3	4	5	6	7	8
HEXADECANE	85	15						
CUMENE		82	17					
DICHLOROBIPHENYL	25	69	5					
ACENAPTHENE		69	31					
TETRACHLOROETHANE		81	19					
o-NITROTOLUENE			30	70				
BENZALDEHYDE			22	75	3			
DIHEXYL ETHER			18	77	4			
N-METHYL ANILINE					3	94	2	
QUINOLINE						100		
DIETHYL PHTHALATE						100		
2-ETHYL HEXANOL						99	0.7	
PHENOL						100		

Figure 4. % Distribution in LC fractions (ref. 9).

is 700. A $1,600 cost increase on 700 samples amounts to $1.7 million. In fact, since four of the seven SASS subsamples usually contain no significant amount of organic material, the expensive part of the scheme is seldom reached. The potential worst case cost must, nonetheless, be seriously considered.

The second strategical problem encountered when considering LRMS for inclusion in Level 1 is that the technique appears to be an "overkill" approach to what was originally a very modest analytical goal. In other words, one probably doesn't need that much information at Level 1 in order to make the necessary decisions. At present, LRMS is included in Level 1 as an option to be used on an "as needed" basis.

It should also be briefly discussed why LRMS is employed rather than the more powerful high resolution mass spectrometry (HRMS) or the more popular gas chromatography/mass spectrometry (GCMS). HRMS is roughly 4 times as expensive as LRMS. The detailed information and compound specificity available from this technique are far beyond the original goal of Level 1, and HRMS is not readily available for the quantity of samples envisioned. GCMS is also more expensive than LRMS and it has the added disadvantage of detecting only chromatographable materials. Both HRMS and GCMS are considered excellent Level 2 techniques.

ILLUSTRATIVE LEVEL 1 DATA

Level 1 SASS subsamples will typically involve results from extraction of particulate, porous polymer, or condensate. An example of this type of data for an electric arc furnace particulate sample is discussed below.

ELECTRIC ARC FURNACE PARTICULATE

Sample Treatment

Particulate (11.500 g) was extracted for 8 hours with 100 ml of methylene chloride in a Soxhlet extractor. Total chromatographable organic analysis (TCO) of the crude extract indicated 1 mg/ml of the C_7 - C_{16} boiling range. Gravimetric (Grav.) analysis indicated an addi-

TABLE 1

LEVEL 1 LC COLUMN RECOVERIES

Fraction	Weight, mg
1	7.2
2	1.5
3	2.0
4	1.9
5	1.8
6	3.3
7	1.4
8	0.1

tional 13.8 mg of organic material present in the extract. The initial TCO + Grav. showed that the sample could be taken to dryness in the later steps of Level 1 without significant loss of sample.

Sample Fractionation

The recovered weights of material from the Level 1 LC column, that resulted from applying the total extracted sample (evaporated to dryness), are given in Table 1.

Infrared Analysis

Infrared results from fraction 6 were the most valuable. Strong or medium bands are reported in Table 2 with their assignments.

The IR of fraction 1 contained only hydrocarbon bands. The spectrum of fraction 3 contained bands at 2925, 2915, and 2830 cm^{-1}, indicative of aliphatic substitution. Infrared analysis of fractions 3 through 7 showed that the organic content of the sample was aromatic in nature with a variety of functional groups including multiple ring structures and oxidation products such as ketones and acids. No LRMS was performed on these samples since the quantity of material in any of the fractions was less than the threshold amount.

CONCLUSION

The objective in Level 1 organic analysis is to provide a cost effective screening scheme for source assessment. The electric arc furnace particulate example above shows many of the benefits of this approach. In particular, that all

TABLE 2

INFRARED BAND ASSIGNMENTS (FRACTION 6)

Band, cm^{-1}	Assignment
3500	A broad band indicating hydroxyl.
1710	Aromatic or conjugated ketone.
1510	Aromatic carbon stretch.
1455, 1460, 1380	Carbon/carbon scissor and wag.
830, 750	Substituted aromatic.

fractions from the LC separation after the second fraction are aromatic in nature and that the boiling point range for the sample is greater than C_{16} shows that the source potentially emits polycyclic organic material (POM) in the toxic and carcinogenic range. The weight and class distribution in the fraction causes the source to be of further interest. Level 2 analysis is indicated for POM by GC/MS or HPLC in combination with LRMS or HRMS.

REFERENCES

1. J. A. Dorsey, L. D. Johnson, R. M. Statnick, and C. H. Lochmuller, "Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1", EPA-600/2-77-115 (NTIS No. PB-268 563), June 1977.
2. R. M. Statnick and L. D. Johnson, "Measurements Program for Environmental Assessment", *Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II* (December 1975, Hollywood, Florida), EPA-600/2-76-149 (NTIS No. PB-257 182), June 1976.
3. J. W. Hamersma and S. L. Reynolds, "Field Test Sampling/Analytical Strategies and Implementation Cost Estimates: Coal Gasification and Flue Gas Desulfurization", EPA-600/2-76-093b (NTIS No. PB-254 166), April 1976.
4. J. Vlahakis and H. Abelson, "Environmental Assessment Sampling and Analytical Strategy Program", EPA-600/2-76-093a (NTIS No. PB-261 259), May 1976.
5. J. W. Hamersma, 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.
6. D. B. Harris, W. B. Kuykendal, and L. D. Johnson, "Development of a Source Assessment Sampling System", presented at Fourth National Conference on Energy and the Environment, Cincinnati, Ohio, October 1976.
7. C. H. Lochmuller, "Analytical Techniques for Sample Characterization in Environmental Assessment Programs", *Symposium Proceedings Environmental Aspects of Fuel Conversion Technology, II,* (December 1975, Hollywood, Florida), EPA-600/2-76-149 (NTIS No. PB-257 182), June 1976.
8. P. W. Jones, A. P. Graffeo, R. Detrick, P. A. Clarke, and R. J. Jakobsen, "Technical Manual for Analysis of Organic Materials in Process Streams", EPA-600/2-76-072 (NTIS No. PB-259 299), March 1976.
9. Arthur D. Little, Inc., Monthly Progress Report on EPA Contract 68-02-2150, April 1977. To be published in a forthcoming EPA report.

APPENDIX A
SELECTED LEVEL 1 PROCEDURES

A.1 *Procedure for Liquid Chromatography Column Preparation*

Column: 200 mm x 10.5 mm ID, glass with Teflon stopcock.

Adsorbent: Davison Silica Gel, 60-200 mesh, Grade 950, (Fisher Scientific Company). This adsorbent is activated at 110°C for 2 hours just prior to use. Cool in a desiccator.

A.1.1 Dry-pack the chromatographic column, plugged at one end with glass wool, with 6.0 g of freshly activated silica gel. A portion of properly activated silica gel weighing 6.0 ± 0.2 g occupies 8 ml in a 10 ml graduated cylinder. Vibrate the column for 1 minute to compact the gel bed. Pour pentane into the solvent reservoir positioned above the column and let the pentane flow into the silica gel bed until the column is homogeneous throughout and free of any cracks and trapped air bubbles*. The total height of the silica bed in this packed column is 10 cm. The solvent void volume of the column is 2 to 4 ml. When the column is fully prepared, allow the pentane level in the column to drop to the top of the silica bed so that the sample can be loaded for subsequent chromatographic elution.

Table A1 shows the sequence of the chromatographic elution. In order to ensure adequate resolution and producibility, maintain the column elution rate at 1 ml per minute.

A.1.2 *Loading Sample on the Column*

Place 1 - 5 ml of CH_2Cl_2 extract containing 15 - 100 mg (preferably 100 mg) of solute (TCO + GRAV) in a graduated centrifuge tube or K-D receiver. Add 200 mg of silica gel prepared as for the LC column. Evaporate if necessary to reduce volume to 1 ml. Add 1 ml of hexane and mix by gentle agitation. Again reduce the volume to 1 ml by evaporation. Add 1 ml more of hexane and mix. Again reduce the volume to 1 ml. Transfer the hexane and silica gel to the top of the previously prepared LC column.

Run the column as directed, rinsing the graduated receiver with fresh solvent as they are introduced in the elution sequence.

A.1.3 *Chromatographic Separation into Eight Fractions*

The volume of solvents shown in Table A1 represents the solvent volume collected for that fraction. If the volume of solvent collected is less than the volume actually added due to evaporation, add additional solvent as necessary. In all cases, however, the solvent level in the column should be at the top of the gel bed (i.e., the sample-containing zone) at the end of the collection of any sample fraction.

After the first fraction is collected, rinse the original sample, weighing the funnel with a few ml of the fraction 2 solvent (20% methylene chloride/pentane) and carefully transfer this rinsing into the column. Repeat as necessary for fractions 3 and 4.

A.2 *Total Chromatographable Organic Analysis (TCO)*

Analyze a 1 μl aliquot of solution by GC using a flame ionization detector. A 6 ft x 1/8 in. O.D. column of 10% OV-101 on 100/120 mesh Supelcoport has been used successfully for this analysis. Other silicon phases (OV-1, etc.) may work as well, but a 10% loading is recommended. The GC should be operated isothermally at about 30° C — or room temperature — for 5 minutes after sample injection and then programmed at approximately 20°C per minute to 250°C and held at 250°C as long as necessary for complete elution of sample.

Integrator should be set to begin integration at a time intermediate between the hexane (C_6) and heptane (C_7) peak maxima (i.e., $C_{6.5}$) and terminate at the peak maxima of the heptadecane (C_{17}) peak, as determined from calibration standards. In this manner the integrated area will cover material in the boiling range of C_7 - C_{16}.

Calibration should utilize a mixture containing a homologous series of hydrocarbons from C_7 to C_{16}. Standards should be prepared to cover the concentration range to be studied.

*A water jacketed column run between 18 and 22°C will help avoid this problem.

TABLE A1

LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

No. Fraction	Solvent Composition	Volume Collected, ml
1	Pentane	25
2	20% Methylene chloride in pentane	10
3	50% Methylene chloride in pentane	10
4	Methylene chloride	10
5	5% Methanol in methylene chloride	10
6	20% Methanol in methylene chloride	10
7	50% Methanol in methylene chloride	10
8	Conc. HCl/Methanol/Methylene chloride (5 + 70 + 30)	10