ENVIRONMENTAL ASSESSMENT SAMPLING AND ANALYSIS: PHASED APPROACH AND TECHNIQUES FOR LEVEL 1

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2. Environmental Protection Technology
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This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

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ENVIRONMENTAL ASSESSMENT SAMPLING AND ANALYSIS: PHASED APPROACH AND TECHNIQUES FOR LEVEL 1

by

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SECTION I

HISTORICAL DEVELOPMENT AND OVERVIEW
OF THE PHASED APPROACH

INTRODUCTION

A sampling and analytical approach has been developed for

conducting environmental source assessments of the feed, product,

and waste streams associated with industrial and energy processes.

The primary intent of this document is to present an overview of:

the historical development of the strategy, the concepts employed,

the measurement techniques applied, and the costs of program imple-

mentation (see Cost Information, page 33). No attempt will be made

to list the myriad details that must be considered: these guidelines

will be supported by a series of forthcoming technical and pro-

cedural manuals.

Before discussing the basic concepts, it seems appropriate to

first outline the components of an environmental source assessment

program. As used in this document and supporting manuals, an environ-

mental source assessment contains: (1) a systematic evaluation of the

physical, chemical and biological characteristics of all streams associ-

ated with a process; (2) predictions of the probable effects of those

streams on the environment; (3) prioritization of those streams rela-

tive to their individual hazard potential, and; (4) identification

of any necessary control technology programs. These components are

depicted schematically in Figure 1. An environmental source assessment

program addresses, to the maximum extent possible, the identification
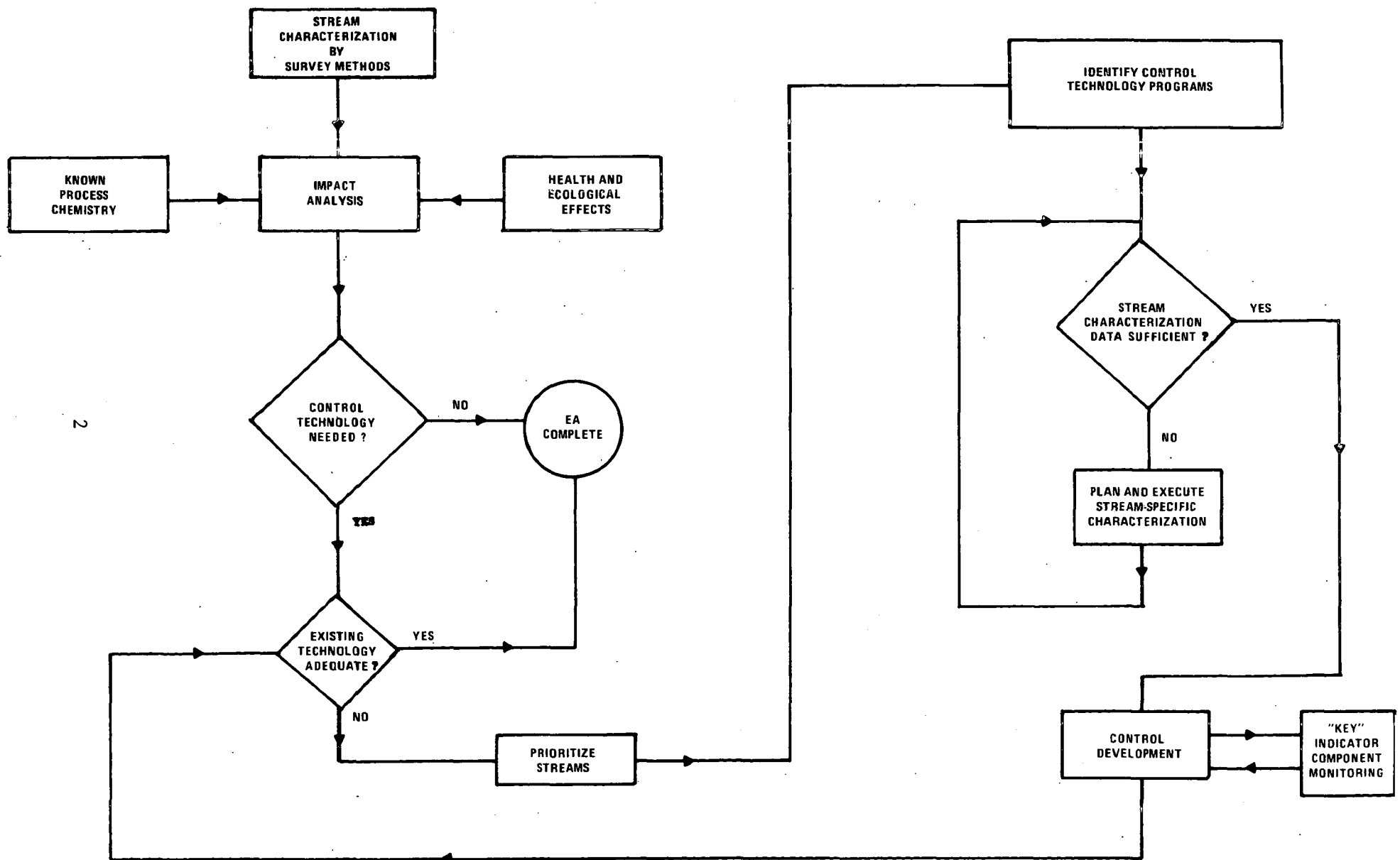
Figure 1. Flowchart of an environmental assessment process.

of all potential air, water, and terrestrial problems, both for

pollutants for which specific standards have been set <u>and</u> for

pollutants that are suspected to have deleterious effects on

the environment and that may be subject to future regulations. The

ultimate goal of an environmental source assessment is to ensure:

(1) that the streams from a given processing scheme will be

environmentally acceptable, or (2) that adequate control technology

either exists or can be developed.

Since an environmental source assessment study must characte-

rize the total pollution potential of all waste streams, the sampling

program must be much more extensive than those generally conducted

for the acquisition of process or control engineering data. The

assessment sampling is more complete in that all waste streams

must be sampled, and no attempt is made to limit sampling to a se-

lected number of process streams. The sampling is also more

comprehensive in that <u>all</u> substances of potential environmental

concern must be detectable above some minimum level of concern.

This comprehensiveness is in direct contrast to the more narrowly

defined lists of major stream components utilized for process

engineering measurement programs. These requirements of complete-

ness and comprehensiveness call for a strategy of approach where

philosophy and structure ensure the maximum utilization of

available resources.

Information Effective Strategies

Two clearly distinct strategies of approach to an environmental assessment sampling and analysis program which would satisfy the requirements for comprehensive information are the direct and phased approaches. In a <u>direct</u> approach, all streams would be carefully sampled and the samples subjected to complete detailed analysis for all detectable components at an overall accuracy of $\pm$ 50 per cent. In a <u>phased</u> approach, all streams would first be surveyed using simplified, generalized sampling and analytical methods which would permit their ranking on a priority basis (Level 1) i.e., very hazardous streams would be distinguished from those less hazardous or relatively innocuous in nature. Level 1 information is anticipated to be accurate to a factor of $\overset{+}{-}$ 2. Detailed sampling and analysis (Level 2) would then be applied first to streams ranked in the highest priority by the Level 1 survey, and other streams would be addressed in descending order of potential hazard. Another phase, initiated after consideration of Level 1 and 2 results, would involve the continuous monitoring of "key" indicator materials to evaluate long-term process variability (Level 3).

It should be clear that any partially direct approach (e.g., the use of predetermined lists of significant compounds) violates the complete and comprehensive requirements of either the direct or the phased environmental assessment philosophy and therefore is not an alternative to either approach. Similarly, <u>a priori</u>

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judgements based on process chemistry, thermodynamics, etc. are
not acceptable practices in this context.

Cost Effectiveness -- Direct and Phased Approaches

Since both the direct and phased (Level 1, 2, 3) approaches
offer, at least in principle, equal promise for ultimate success
(i.e., comprehensiveness and complete characterization), it is worth-
while to examine their relative resource requirements. Studies
were conducted by the staff of the Process Measurements Branch of
EPA's IERL-RTP with the objective of comparing the costs of direct
and phased (with elimination of low priority streams) sampling and
analysis approaches. Details of these studies will be reported
elsewhere, but it is interesting to consider the final estimates
for two unit operations -- a limestone wet scrubber and full-scale
low-BTU coal gasifier. The scrubber involved seven feed or waste
stream sampling sites. The gasifier contained a total of 70 iden-
tifiable stream sampling points. A comparison of the total estimated
costs for both processes by both approaches is shown in Table 1.

Table 1. ESTIMATED TOTAL COSTS OF DIRECT
          VS PHASED APPROACHES TO SAMPLING
          AND ANALYSIS

Process	Phased (Total 1,2)	Direct
Limestone Wet Scrubber	$ 350,000	$ 500,000
Coal Gasifier	$ 725,000	$1,450,000

In both cases, the phased approach was found to be more cost effective than the direct approach even though the scrubber and coal gasifier differ markedly in size, complexity, basic technology, and total cost of sampling and analysis. The cost advantages of the phased sampling and analysis approach were found to be approximately proportional to the complexity of the process being sampled. The phased approach resulted in a 50 percent reduction in costs over the direct approach for the gasifier (70 streams), and the corresponding savings for the wet limestone scrubber were 30 percent (7 streams). Within the phased approach, the initial (Level 1) sampling and analysis costs were shown to be 10 percent of the total cost of the phased effort. Thus, many qualitative judgements, including whether or not a full-scale endeavor is at all necessary, can be made at low cost before a commitment is made to initiate a detailed (Level 2) assessment.

This actual resource savings is only one aspect of justification for the phased scheme. As the result of information developed in Level 1, a significant improvement in sampling can be anticipated at Level 2. It is doubtful that equal data could actually be acquired in a direct approach due to the lack of the very necessary learning processes involved in difficult source sampling and analytical projects.

SAMPLING PROGRAMS IN A PHASED APPROACH

Based on the results of the studies mentioned, the most cost-effective approach clearly is one in which detailed sampling is performed only on those streams demonstrated to be potentially hazardous by a generalized survey program. Further, it has been noted that it is not sound practice to attempt to define a detailed sampling program until: (1) the general characteristics of the stream in question have been evaluated, and (2) the nature of any unfavorable sampling system/sample interactions has been considered (e.g., chemical reaction, volatility loss). Hence, an effective sampling program involves a series of reiterative tests in which each iteration enhances the source assessment by focusing resources and efforts on the pollutants and streams of concern. At the end of each refinement and before further resources are expended, the output can be compared for equivalency to the goals of the overall program itself.

Level 1 Sampling

Level 1 sampling stresses the concept of completeness by presuming that any and all streams leaving the process will be sampled unless empirical data equivalent to Level 1 programmatic output already exists. Further, Level 1 sampling is not predicated on a priori judgements as to the composition of streams. The techniques utilized presume that whatever prior knowledge is available, at best, is incomplete. Predictive and extrapolative

techniques employed during source assessments serve as a check on the empirical data and not as a replacement for it.

Level 1 sampling systems are therefore envisioned to permit collection of all substances in the stream at a reasonably high level of efficiency. They do not necessarily produce information as to specific substances or their chemical form. For example, if sulfur-containing gases are in the gas stream, Level 1 sampling will separate and retain all particulates and vapor-phase organic and inorganic sulfur compounds, and the distinction between particulate and gaseous forms can be made. Although Level 1 is not designed to preserve the specific sulfur compound identity, in many cases a reasonable specific compound identification may result. However, conceptually, the identification is not necessary in judging the success of Level 1.

Further, Level 1 sampling programs are designed to make maximum use of existing samples and stream access sites. While some care must be exercised to ensure that the samples are not biased, the commonly applied concepts of multiple point, isokinetic or flow proportional sampling are not rigidly adhered to. Normally a single sample of each stream should be collected under average process operating conditions or, alternatively, under each condition of interest. These samples should be time-integrated over one or more process cycles. When a series of discrete samples result, they are combined to produce a single "average" for analysis, and the average is considered as representative of the total process cycle.

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Level 2 Sampling

Level 2 sampling programs are directed toward a more detailed representation of stream composition. They are not as "inclusive" as Level 1 in that resources are expended to improve information only on streams of a critical nature. Additional sampling of other streams is deferred because Level 1 information has indicated a less significant level of environmental impact. Level 2 sampling is optimized for specific compounds or classes of compounds contained in the streams sampled. It also provides a more quantitative description of the concentrations and mass flow rates of the various substances in the stream.

Level 2 sampling must be considerably more refined than Level I since it is being conducted on streams which have already been identified by Level 1 results as having potentially adverse environmental effects. One primary refinement will be the need for more rigorous attention to selection and preparation of sampling sites. Additionally, adherence to procedures for acquiring a representative sample must be incorporated into the test procedures. Level 2 sampling should also provide for replication of samples in order to further improve accuracy and be more representative.

In many cases, Level 2 sampling will require not only more care in use but also modifications of Level 1 equipment and/or the application of entirely new methods. Such cases result from the

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necessity to identify more definitively the materials which

produce the adverse environmental problems. For example, if

Level 1 has indicated a high concentration of sulfur-containing

species, Level 2 sampling must be specifically designed to

provide isolation of the sulfur-containing materials into appro-

priate fractions which can be analyzed for individual compounds

or compound classes.

Level 3 Sampling

At Level 3, emphasis is placed on the variability of stream

composition with time and process or control system parameters.

Having determined at Level 1 that a stream is environmentally

unacceptable and at Level 2 what the unacceptable components

are, it is now necessary to define accurately the range of values

to be expected and the effectiveness of a control process if control

equipment is installed. An effective Level 3 sampling program

is designed to monitor a limited number of selected compounds or

compound classes.

Level 3 sampling is designed to provide information over

a long period of time. To be cost effective, such programs must

be tailored to the specific requirements of each stream being

monitored. Based on the information developed at Level 2,

specialized sampling procedures can be designed to track key

indicator materials at frequent intervals. If at all possible,

Level 3 should also incorporate continuous monitors where appropriate.

During Level 3 programs, it is anticipated that Level 2
sampling will be conducted at predetermined intervals to check
the limited Level 3 information. Further, recommended procedures
for compliance testing should be introduced into the program at a
time appropriate to the status of the process or control technology
development.

ANALYTICAL METHODOLOGY IN A PHASED APPROACH

During an environmental source assessment, the analytical
methods applied will vary from relatively simple, manual wet chemistry
to highly complex instrumental techniques. Analyses proceed from
general, broadly applicable, survey methods to more specialized
techniques tailored to specific component measurements. This very
broad range requirement has been structured to adhere to the same
level concept described for the sampling program. At each phase
of the analytical program, the depth and sophistication of the
techniques are designed to be commensurate with the quality of the
samples taken and the information required. Hence, expenditure
of analytical resources on screening type samples from streams of
unknown pollution potential is minimized.

Level 1 Analysis

Level 1 sampling provides a single set of samples acquired to
represent the average composition of each stream. This sample
set is separated, either in the field or in the laboratory, into
solid, liquid, and gas-phase components. Each fraction is

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evaluated with survey techniques which define its basic physical, chemical, and biological characteristics. The survey methods selected are compatible with a very broad spectrum of materials and have sufficient sensitivity to ensure a high probability of detecting environmental problems.

In Level 1, the analytical techniques and instrumentation have been kept as simple as possible in order to provide an effective level of information at minimum cost. Each individual piece of data developed adds a relevant point to the overall evaluation. Conversely, since the information from a given analysis is limited, all the tests must be accomplished to provide a valid assessment of the sample.

Physical analysis of solid samples is incorporated into Level 1 because the size and shape of the particles have a major effect on their behavior in process streams, control equipment, atmospheric dispersion, and the respiratory system. In addition, some materials have characteristic physical forms which can aid in their identification. Chemical analyses to determine the types of substances present are incorporated to provide information for predicting: control approaches, atmospheric dispersion/transformation, and potential toxicity of the stream. Finally, because prediction of hazard based on physical and chemical analyses alone is subject to many uncertainties, biological assay techniques are incorporated as a measure of the potential toxicity.

Level 2 Analysis

The analytical procedures applied at Level 2 may be extensions of the Level 1 procedures. In most cases, however, information developed at Level 1 will provide background for selection and utilization of more sophisticated sampling and analysis techniques. Since these techniques will require a major investment in equipment and a well-trained staff, Level 2 analyses will probably be most effectively accomplished by a limited number of selected laboratories.

Because Level 2 analyses must positively identify the materials in sources which have already been defined as causing adverse environmental effects, these analyses are the most critical of all three levels. It is equally important, however, that the analyses be conducted in an information-effective manner. This is because increasing specificity and/or accuracy result in cost escalations which are, at best, exponential rather than proportional. Due to the multiplicity of analytical techniques required and the potential for unnecessarily high expenditures, Level 2 analyses should be managed and interpreted by experienced analytical personnel working in well-equipped laboratories. Furthermore, the analyses must be conducted with a full awareness of the information requirements of an environmental assessment program.

It is evident from the preceding comments that Level 2 analyses cannot be conducted via a prescribed series of tests. Each sample

will require the analyst to select appropriate techniques based on the information developed in Level 1 and the information requirements of the assessments. Several attempts have been made to formulate a generalized scheme which proceeds through a complex series of logical "if-then" steps; however, no optimized approach is presently available. Whatever scheme is utilized for Level 1, it must contain physical, chemical, and biological analyses. In the absence of a general scheme, Table 2 indicates the types of analyses which are applicable at Level 2.

Level 3 Analysis

The analytical procedures for Level 3 are specific to the stream components being monitored, and it is not possible to define the exact form they may take. Level 3 analyses are oriented toward the time variation in the concentrations of key indicator materials. In general, the analysis will be optimized to a specific set of stream conditions and will therefore not be as complex or expensive as the Level 2 methods. Both manual and instrumental techniques may be used, provided they can be implemented at the process site. At Level 3, continuous monitors for selected pollutants should be incorporated in the analysis program as an aid in interpreting the data acquired through manual techniques.

The Level 3 analysis program should also include the use of Level 2 analysis at selected intervals as a check on the validity of the key indicator materials to reflect process variability.

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Table 2. ANALYTICAL CHEMICAL TECHNIQUES APPLICABLE
IN LEVEL 2 FOLLOWING LEVEL 1 SURVEY OF STREAM CONTENTS[*]

Category A

Wet Chemical Methods

(e.g., SO_4, NO_3, F,

total phenolics)

Elemental Analysis

Spark-Source Mass Spectrometry

Atomic Absorption Spectrometry

Arc and Spark Emission Spectrometry

Neutron Activation Analyses

X-Ray Fluorescence

Organic Materials

Infrared Spectrometry

G. C. - Mass Selective Detector

G. C. - Selective Detector

(e.g., Flame Ionization, Flame

Emission, Electron Capture)

Chemi-Ionization Mass Spectrometry

Category B

Separation Techniques

High-Performance Liquid

Chromatography

Gas Chromatography

Ion Exchange

Solvent Extraction

Structure Elucidation

Nuclear Magnetic Resonance

High-Resolution Mass Spectrometry

Photoelectron/Inner Shell Electron

Spectrometry (Surface Inorganics)

Infrared Spectrometry

Quantitative Measurement

If not achieved in Separation

or Structure Elucidation,

utilize Category A.

[*] This is not an all inclusive or an exclusive list. Choice of

the most cost/information effective methods will vary from

sample to sample.

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SECTION II

LEVEL 1 METHODOLOGY AND COMPONENTS

INTRODUCTION

In Section I, a three-level phased approach to a cost and information-effective measurement program for environmental assessment studies was presented. In general, the intent of each phase is the measurement of the mass flow rates of primary pollutant classes -- either out of the envelope containing the process or out of the plant of which the process is one part. The strategy which has been developed includes characterization of feed streams to provide a rough material balance and to determine if feedstock modification is an effective control approach. The characterization also extends to the product streams whenever they may directly affect the environment at the next step of usage.

Level 1, the principal subject of this section, is structured to produce a cost-effective information base for prioritization of streams and for planning any subsequent programs. It seeks to provide input data to support evaluation of the following questions:

a. Do streams leaving the processing unit have a finite probability of exceeding existing or future air, water, or solid waste standards or critieria?

b. Do any of the streams leaving the processing unit contain any classes of substances that are known or suspected to have adverse environmental effects?

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c. Into what general categories (classes) do these

adverse substances fall?

d. What are the most probable sources of these

substances?

e. Based on the adverse effects and mass output

rates, what is the priority ranking of streams?

f. For streams exhibiting potential environmental

effects, what is the basic direction that control

strategies are likely to follow?

The Level 1 measurement program provides information on the
physical characteristics, chemical composition, and biological
effects of a given stream.

These program components produce data which permit both the
identification of existing problems and the evaluation of the
possible adverse environmental effects of the streams. The
measurement techniques do not attempt the quantitative determination
of compliance with existing standards; however, they do provide re-
sults that can be used both for semiquantitative evaluation of process
compliance and for planning subsequent sampling and analysis programs.

It is desirable that the Level 1 measurement methods be
designed to ensure comparability of information from a wide range
of processes. Present indications are that a reasonably specific
set of procedures can be defined for Level 1 studies. The proposed
methodology is applied to all streams from a given source during a

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single, comprehensive field test period. This approach is sound
and reasonable since it ensures comparability and internal con-
sistency in Level 1 data by removing bias due to measurement proce-
dures and to feedstock or process variations that might occur over ex-
tended sampling periods. The following discussions are a general
description of the techniques applied. A more detailed procedures
manual is being prepared to provide specific information on each
aspect of Level 1.

Level 1 Sampling Effort

The goal of the Level 1 sampling effort is to acquire for subse-
quent analysis, a sample from each process feedstock stream, each pro-
cess waste stream, and each process product stream. In addition to sample
acquisition, sufficient process data must be acquired to permit cal-
culations such as mass emission rate and mass emission rates per unit
of product. These data must be acquired during the sample acquisition
phase, and the test program should establish the flow rate of each
stream sampled. The quality of these data needs only to be comparable
to the sampling error and can be obtained from direct measurements,
from operator log sheets, or from indirect approaches such as fan and
pump curves.

Sample Acquisition

It is consistent with the philosophy of an environmental assess-
ment at Level 1 that the sampler should not prejudge the chemical
and/or physical nature of any stream. For example, a flue gas stream

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is always assumed to contain inorganic and organic gases as well as inorganic and organic entrained particulates. The subsequent physical and chemical analyses will then be used to establish the presence or the absence of any constituent.

To provide this type of unbiased sampling, the acquisition of gas samples requires the use of a sampling train designed specifically for environmental assessment sampling. The Source Assessment Sampling System (SASS) (shown schematically in Figure 2) will be used to sample at 90-150 lpm (3-5 scfm) and collect both solids and vapors. The entrained particulates are fractionated into four sizes: > 10 μm, 3-10 μm, 1-3 μm, and < 1 μm. Vapor-phase organic materials are adsorbed on a solid sorbent, and the inorganic vapors are retained in the chemically active impinger solutions.

Because it is impossible to predict the concentration of a constituent in the gas stream at the start, sampling is based on the minimum volume of gas necessary to provide detection of materials in the analytical scheme. A minimum of 30 m^3 (1000 ft^3) is sufficient to ensure detection of materials at approximately 1 mg/m^3. Utilizing the 90-150 lpm SASS train will require a sampling time of 3.5 to 5.5 hours.

The solid sorbent used in the SASS train does not collect, quantitatively, materials whose boiling points correspond to those of the less than C_6-hydrocarbons with optimum efficiency. Therefore,
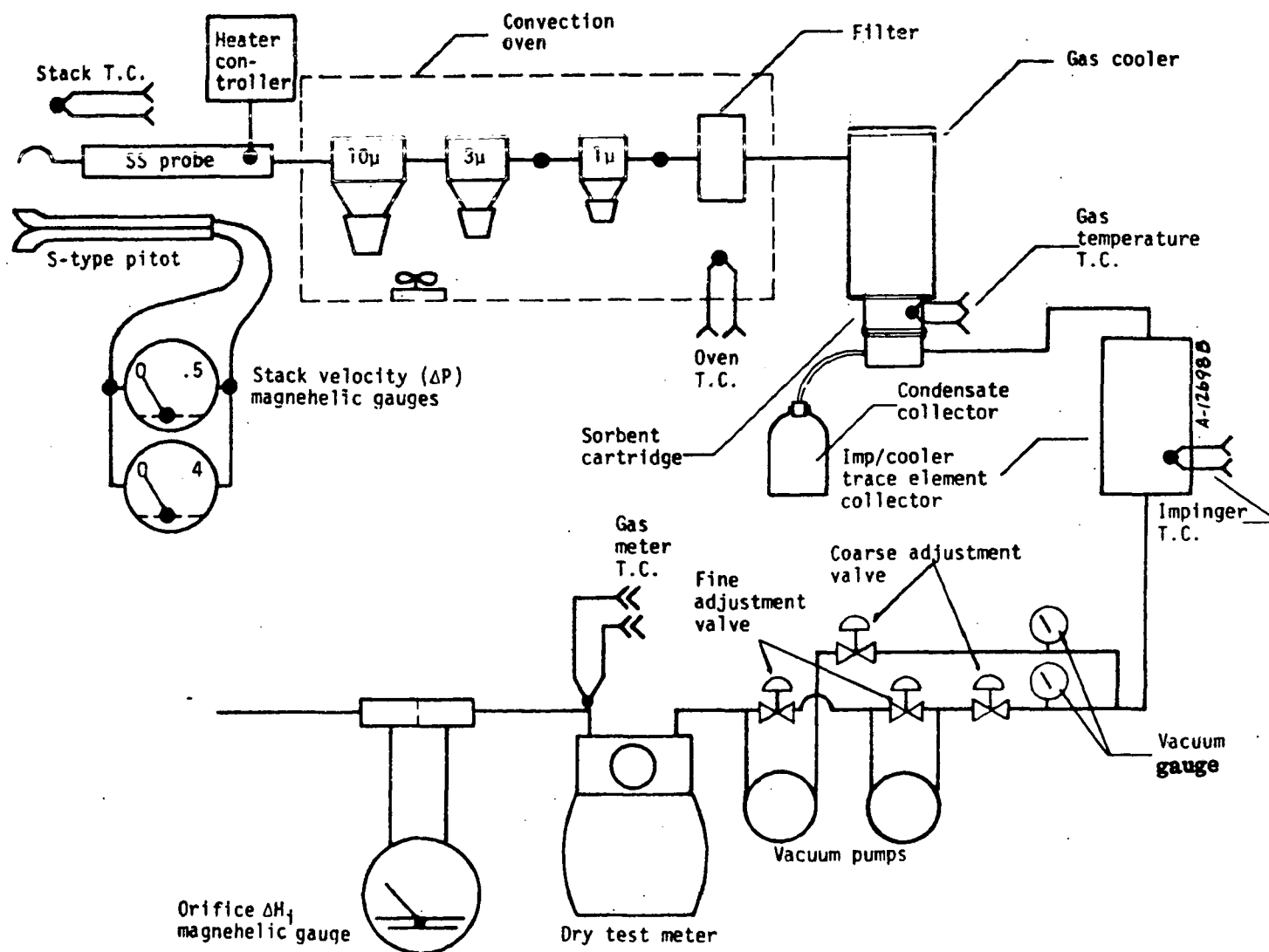
Figure 2. Source assessment sampling system train.

a gas sample is acquired in addition to the SASS samples from each gas stream. These gas samples are analyzed in the field by gas chromatography utilizing multiple column/detector methodology.

For solids and liquids, the sampling methodologies are also kept at a minimum level compatible with the Level 1 analyses. Liquid samples are acquired from existing taps in lines or with simple dippers from open streams. Solid sampling is effected with coring devices for piles and with a shovel for moving streams. General requirements are listed in Table 3.

Table 3. REQUIREMENTS FOR STREAM SAMPLING

Stream	Sample Size	Location	Sampling Procedure
Gas	30 m^3	Ducts, stacks	SASS train
Liquid	10 liter	Lines or tanks	Tap or valve sampling
		Open free-flowing streams	Dipper method
Solids	1 kg	Storage piles	Coring
		Conveyors	Full stream cut

A further sampling category included in Level 1 is fugitive emissions. A fugitive emission is any solid, liquid, or gaseous emission which is not released through ducts, pipes, stacks, etc. of a regular cross-sectional area. General techniques that are applicable to such emissions are listed in Table 4.

Table 4. FUGITIVE EMISSIONS SAMPLING TECHNIQUES

Sampling Technique	Applicable to	Description
SASS	Gases, Dusts	Sample at emission point
Upwind/Downwind	Gases, Dusts	Establish a sampling network upwind and downwind of the source
Plug Reservoir	Liquids	Establish network around source to sample runoff

In many cases, the upwind/downwind technique may also be used to isolate a specific process from the general plant background. This requires mobile units which can be kept downwind of the fugitive source.

Manpower Associated with Sample Acquisitions

The acquisition time per sample -- which includes equipment setup time, sample acquisition time, and equipment tear-down and cleanup time -- has been estimated as a function of sample type and is given in Table 5. These estimates do not include site preparation times or travel. The estimated level of effort per stream is based upon the use of an experienced field sampling team.

Table 5. MANPOWER ASSOCIATED WITH SAMPLE ACQUISITION

	Manhours/Stream	Cost*
Particulate & Gases	12	$ 360
Liquid	1	30
Solid	1	30
Fugitive Particulate	15	450

*Assuming $30/mhr

LABORATORY ANALYSIS

The information that will be available for the prioritization
of process streams will come from analyses carried out on samples
collected via the previously described methods. Some of the analyses
will be performed as part of the sampling team effort (e.g., on-site
gas chromatography); others require laboratory conditions that could
be achieved in the field only at high, unwarranted expense. The
general analysis scheme is divided into three stages (physical and
chemical characterization, and biological hazards) that have been
designed to yield a maximum amount of useful complementary infor-
mation at reasonable cost. The scheme yields relevant information
on all pollutants including those covered by emission standards.

The first stage involves the physical characterization of solid
and particulate matter, including such items as morphology and particle
size distribution. The second deals with the chemical characterization

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of samples and sample extracts and includes the determination

of elemental distribution from both qualitative and semi-quantitative

viewpoints. Organic material is separated into fractions that can

be assayed on a weight basis. The third stage involves the deter-

mination of biological hazards in the form of in vitro measurement

of cytotoxicity, mutagenicity, and ecological effects in the form

of selected plant and animal responses. Figure 3 shows flow charts

of the analysis scheme and the estimated cost of each analysis scheme

of field samples.

Physical Characterization

Level 1 physical characterization of solids suspended in gas

streams is carried out initially in the field utilizing the cyclone

system in the SASS train. The solids are weighed in the laboratory

and then combined into a > 3 μm fraction and a < 3 μm fraction. Optical

photomicroscopic examination is then performed on the two fractions.

In solids from piles, storage bins, etc., the size distribution

is determined using a Coulter Counter. Optical photomicroscopy

evaluation of these samples is also performed to determine particle

morphology.

Chemical Characterization

In Level 1, it is important that no assumptions be made about

the composition of the samples obtained in the field. The recommended

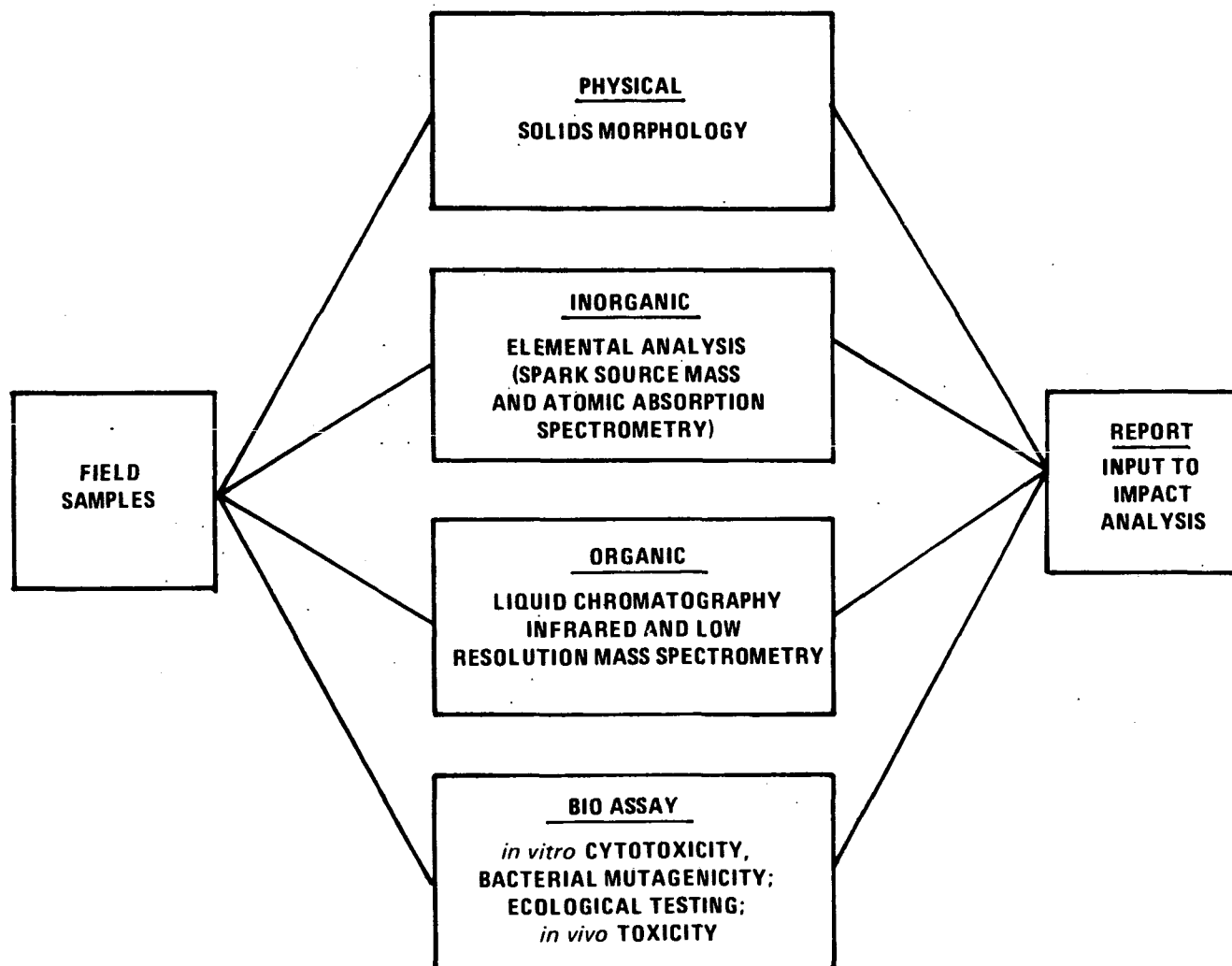analytical procedures are, therefore, designed to be generally

Figure 3. Flow chart of level I scheme.

applicable and to yield information appropriate to the needs

of the stream prioritization strategy. Since the costs of chemical

analysis increase in proportion to the demand for increased quali-

tative differentiation and quantitative precision, the Level 1

procedures do not seek to identify particular chemical compounds

as such. The results of the analysis schemes to be outlined in

this section are combined with the analyses performed by the field

sampling team to form the chemical information output.

It is convenient to divide analytical schemes into the classical

subdivisions of inorganic and organic analyses, despite the fact

that such chemical classes as the organometallics (or metallo-

organics) can be considered in either subdivision. In Level 1

chemical analysis: inorganic analysis involves determination of

elemental composition; organic analysis is the separation of organic

solvent soluble material, by gas and liquid chromatography, into

defined fractions that include the general classes of organic com-

pounds. No classes of compounds or elements have been excluded;

however, no deliberate attempt has been made to optimize any

specific compounds or elements.

Level 1 inorganic analysis utilizes the Spark Source

Mass Spectroscopic technique to achieve qualitative and semi-

quantitative elemental analyses on all solids, particulates,

filterable solids from liquid streams, and evaporated residues

of liquid samples. This technique is used because of its:

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general multielement capability, acceptable detection limits, speed, and cost. An accuracy of a factor of $\pm$ 2 and a detection limit of 1 ppm for all elements analyzed are specified. Since spark-source mass spectrometers are quite complex (fairly expensive instruments that require highly trained operators), the estimated cost of a Level 1 elemental analysis is $300.

The Level 1 organic analysis achieves a semi-quantitative estimate of the predominant classes of organic compounds present in samples taken from process streams. Classes of organic compounds include: paraffins, aromatic hydrocarbons, alcohols, ketones, aldehydes, carboxylic acids, and amines. While it is possible to fractionate complex mixtures into these classes, it is difficult and costly. The Level 1 strategy is to isolate well-defined fractions by conventional liquid chromatography rather than isolate specific classes. Under controlled conditions, the contents of a chromatography fraction (in terms of class types) are predictable. An example of the relation between organic class and chromatographic fraction is illustrated in Figure 4.

Organic extracts of $> C_{12}$ materials are resolved into eight fractions by liquid/solid chromatography on silica gel, utilizing a prescribed series of eight solvent mixtures as elutants. The fractions are evaporated to constant weight by methods that minimize evaporative loss of the constituents of interest. The weight of each fraction is determined to $\pm$ 0.5 mg. As an aid to identification

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        1           2           3           4           5           6           7           8
  ├─────────────┼───────────┼───────────┼───────────┼───────────┼───────────┼───────────┤
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Paraffins

       Aromatic
       Hydrocarbons

              Polyaromatic
              Hydrocarbons

                    Heterocyclic
                    Sulfur Compounds

                       Esters, Alcohols,
                           Ketones

                              Phenols, Amides
                              Carboxylic Acids

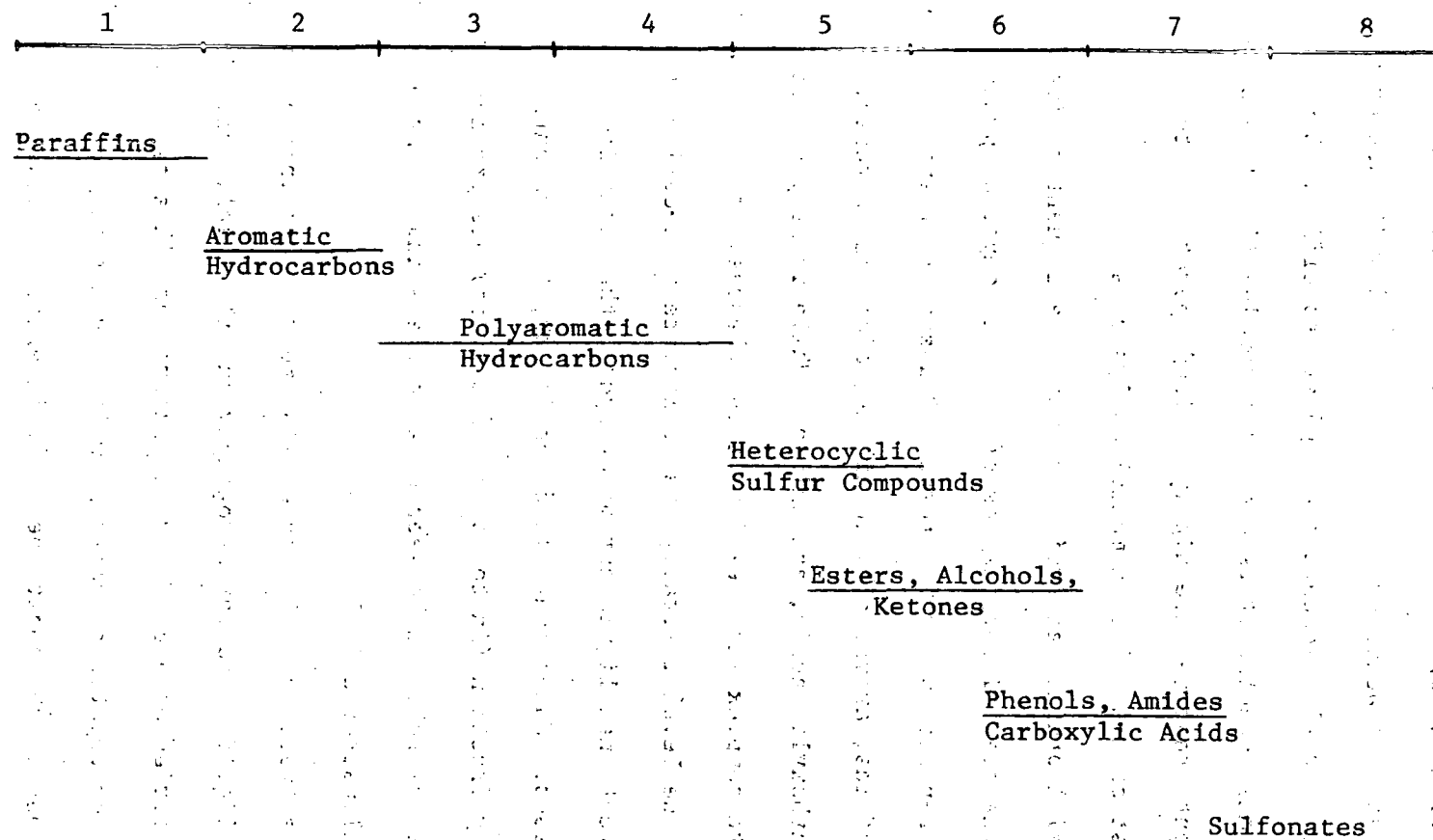   Sulfonates

Figure 4. Liquid chromatographic fractions vs class types.

of the constituents of each fraction, an infrared (IR) adsorption

spectrum is obtained and interpreted. For those fractions whose

mass exceeds a minimum level of concern for source concentration

(i.e., 0.5 mg/nm^3 for stack gases), further analysis is performed

by Low Resolution Mass Spectrometry (LRMS). The total cost of a

Level 1 organic analysis is approximately $500.

Organic analysis of C_7-C_{12} materials which might be lost

during evaporation is conducted using gas chromatographic techniques.

This is done on the sorbent trap extract prior to concentration for

liquid chromatographic separation. The separation is essentially

by boiling point, and compounds are grouped into classes by boiling

point range.

The required level of operator training is that of skilled

technicians capable of following the Level 1 technical and procedural

manual. Interpretation of the infrared and low resolution mass

spectra will require a senior technician trained and experienced

in such tasks.

Chemical analysis of inorganic gases and of low-molecular weight

organic gases is conducted in the field using gas chromatographic

techniques. Nitrogen oxides are also determined using chemiluminescence.

All other analyses are performed in the laboratory.

Determination of Biological Hazards

Biological tests included in the Level 1 analysis scheme are

intended to indicate potential biohazards independently

of chemical analysis. This environmental assessment tool is an important aspect since chemical information, as mentioned earlier, is an ambiguous predictor of biological activity. Level 1 chemical analysis is a search for danger signals; bioassay provides additional indicators. This aspect of the Level 1 analysis strategy is still in development, and the methods described are examples of present thought. The bioassay component is anticipated to extend to methods which assess the terrestrial and aquatic effects of certain process waste streams and fugitive emissions.

Like the chemical analysis, Level 1 bioanalysis must remain relatively simple and inexpensive. For this reason, in vitro or test tube methods are highly advantageous for the first level. The selected methods discussed in this section provide an estimation of acute cellular toxicity and of certain types of mutagenic activity. In addition to being of direct interest, mutagenic behavior is an effective screening indicator for carcinogenic activity. Although not all mutagens are carcinogenic, nearly all carcinogens cause mutagenesis.

An estimate of the acute cellular toxicity is determined by means of the rabbit alveolar macrophage procedure. Although the system presents opportunities for considerably more sophisticated studies, only cell mortality compared to controls has been utilized as part of Level 1. Particulate samples are added, in weighed quantities, to the culture medium and incubated before adding the

test cells. After a second incubation, the number of dead and living cells is determined by dye exclusion techniques. Appropriate tests for water samples and other liquid materials are under consideration.

The recommended test for mutagenesis is carried out using a B. Ames type procedure with selected strains of microorganisms. At Level 1, only one solvent system is employed. Solid samples are dissolved as completely as possible in dimethyl sulfoxide, filtered, and added to the test system. Liquid samples are added to dimethyl sulfoxide and then to the test system.

Skilled technicians, under close supervision of a professional cytologist and bacterial geneticist, are required for the cytoxicity and mutagenicity testing, respectively. Experienced personnel must interpret the test results. To avoid health hazards to the test personnel, laboratories must be well equipped and carefully managed to prevent chemical or biological contamination of samples. For these reasons, this work must be conducted in laboratories approved by EPA health effects programs.

FURTHER USE OF LEVEL 1 SAMPLES

Level 1 samples are anticipated to be used during the early stages of Level 2 sampling and analysis strategy planning. While analysis of the samples by Level 2 methods cannot be considered as a substitute for Level 2, the analysis can provide useful, additional information for Level 2 program development.

For example, if the Level 1 organic analysis suggests the presence of oxygenated hydrocarbons which may include phenols and if other tests indicate the sample is toxic, then a direct analysis for phenolic compounds as a class may be desirable prior to Level 2. This confirmation of phenols would aid in optimizing sampling for these species. However, because Level 1 sampling, sample handling, and storage are not optimized, the data cannot be used to accurately quantify materials detected.

REPORTING

The output from Level 1 testing must provide a basis for the decision to proceed with Level 2 sampling and analysis and must also provide direction to the design of the Level 2 test program. The essential data for this purpose are:

a) Concentration of elements in streams sampled. (This information is derived from SSMS analysis and appropriate volumetric measurements.) Mass emission rates are also necessary for all effluent streams.

b) Weight percentage of total organics found in each chromatographic fraction. (These should also be expressed as mass emission rates for total organics and organics in each fraction.)

c) Preliminary identification of organic species from IR/LRMS.

d) Photomicrograph and description of morphology.

e) Particle size data, if applicable.

f) Gas chromatographic data from field portable unit. In

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addition, the presence and estimation of concentration of volatile materials need to be determined.

g) Estimation of potential acute toxicity and mutagenicity characteristics of all streams subjected to bioanalysis.

h) Volumetric flow rates, production rates, and other appropriate process data at the time of sampling.

Calculations, using Level 1 data, of the quantities of output should be made well in advance of the sampling visit to ensure that essential information is not overlooked.

COST INFORMATION

Estimated costs are summarized below for Level 1 sampling, analysis, and reporting.

a. Site preparation (per site) . . . . $ 250
b. Travel (3-man crew) and shipping 2,650
c. Sampling by stream type (per sample):
   Fugitive Dust 450
   Liquid. 30
   Particulate & Gases 360
   Solid 30
d. Analysis by sample (per sample):
   Gas 1,600
   Liquid. 2,600
   Particulate 4,600
   Solid 1,400
e. Data reduction and reporting 2,500

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16. ABSTRACT
The report discusses a three-level approach to sampling and analysis, and gives details of a Level 1 sampling and analysis phased approach for an environmental source assessment. A research program was initiated to develop a sampling and analytical approach for conducting environmental source assessments of the feed, product, and waste streams associated with industrial and energy processes. An environmental source assessment identifies potential air, water, and terrestrial problems for both regulated (specific standards exist) and unregulated pollutants (future regulations may be necessary). The three-level sampling and analysis approach resulted from this program. Level 1 is a complete survey of all streams, using simplified, generalized sampling and analytical methods which permit priority ranking; i.e., hazardous streams are distinguished from those less hazardous or relatively innocuous in nature. Level 2 is detailed sampling and analysis of the streams ranked in the highest priority by the Level 1 survey. Other streams may then be addressed according to potential hazard. Level 3 involves continuous monitoring of 'key' indicator materials to evaluate the effect on emissions of process variability.

17	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Sampling Analyzing Measurement Industrial Processes Energy	Process Variables Toxicity Bioassay Hazards Ranking	Pollution Control Source Assessment Process Streams Hazard Potential Prioritization	13B 07A,13H 14B 06T 06A 13H 12B

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