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RESPONSES TO COMMENTS ON DRAFT STAGE I REPORT AND DRAFT SUPPLEMENTAL WORK PLAN FOR REMEDIAL INVESTIGATION / FEASIBILITY STUDY HASSAYAMPA LANDFILL HAZARDOUS WASTE AREA MARICOPA COUNTY, ARIZONA

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602) 881-4912
TELEX: 165597 MONTE TUC

CRA Consulting Engineers
CONESTOGA-ROVERS & ASSOCIATES
382 WEST COUNTY ROAD D
ST. PAUL, MINNESOTA 55112
TELEPHONE (612) 639-0913

ERROL L. MONTGOMERY & ASSOCIATES, INC.
CONSULTANTS IN HYDROGEOLOGY
1075 EAST FORT LOWELL ROAD, SUITE B
TUCSON, ARIZONA 85719 (602)881-4912
TELEX: 165597 MONTE TUC
FAX: (602)881-1609

ERROL L. MONTGOMERY, P.G.
JOHN W. HARSHBARGER, P.G., P.E.
DONALD K. GREENE, P.E.
WILLIAM R. VICTOR, P.G.
EDWARD W. PEACOCK, P.G.
RONALD H. DEWITT, P.G.
MARK M. CROSS, P.G.

October 5, 1989

Daniel D. Opalski (T-4-1)
Project Coordinator
U. S. ENVIRONMENTAL PROTECTION AGENCY
Region 9
215 Fremont Street
San Francisco, California 94105

RE: FINAL RESPONSES TO COMMENTS ON DRAFT STAGE I REPORT AND DRAFT SUPPLEMENTAL WORK PLAN FOR HASSAYAMPA LANDFILL

Dear Mr. Opalski:

On July 25, 1989, we received comments via telefax from the U. S. Environmental Protection Agency (EPA) on the draft Stage I Report and the draft Supplemental Work Plan for Stage II, both dated March 13, 1989, for the Remedial Investigation / Feasibility Study (RI/FS) for the hazardous waste area (the Site) at the Hassayampa Landfill, Maricopa County, Arizona. In accordance with subsection VII.C.5 of the Administrative Consent Order (EPA Docket No. 88-08) for the Site, receipt of the EPA comments began a 15-day technical review period during which the Hassayampa Technical Work Group met.

Comments by Arizona Department of Water Resources (ADWR) and Arizona Department of Environmental Quality (ADEQ) on the two draft documents were received on May 9, 1989, and June 12, 1989, respectively. ADWR had no comments. Agency comments were discussed in detail via telephone conversations between Montgomery & Associates, EPA, and ADEQ. We prepared and submitted draft responses to EPA and ADEQ on August 4, 1989. A meeting of the Hassayampa Technical Work Group was held on August 8, 1989, at the EPA offices in San Francisco, California, to discuss the comments and draft responses.

The August 8 meeting resulted in general agreement between EPA, ADEQ, and the Respondents regarding the draft Stage I Report and the draft Work Plan. It was suggested at the meeting that the draft Stage I Report could be considered the final Report if a few selected responses would be revised to reflect the resolutions of the Technical Work Group. For this purpose, a second draft of the responses, dated September 1, was submitted to EPA and ADEQ for review and comment. One modification of the September 1 submittal was requested by EPA; no modifications were requested by ADEQ.

In addition to EPA's written comments, a verbal comment was made by EPA regarding the draft Stage I Report. Table 11c in Volume II of the Report gives Conestoga-Rovers & Associates' (CRA) comparison of downwind air quality at the site to air risk thresholds. A review of the data presented in Table 11c revealed an error. At EPA's request, the Threshold Limit Value (TLV) utilized in Table 11c for the C6 aliphatic hydrocarbon should be the value for n-hexane, which is 180,000 micrograms per cubic meter ($\mu g/m^3$) rather than the 1,800,000 $\mu g/m^3$ reported.

The following documents are attached hereto:

ATTACHMENT 1a: EPA comments, dated July 25, 1989

ATTACHMENT 1b: Final responses to EPA comments

ATTACHMENT 1c: Technical paper by Rowan, Connolly, and Brown, dated 1984

ATTACHMENT 2a: ADEQ comments, dated June 7, 1989

ATTACHMENT 2b: Final responses to ADEQ comments

ATTACHMENT 3: ADWR comments, dated May 4, 1989

ATTACHMENT 4: Proposal by CRA for Stage II air investigation

EPA qualified the representativeness of results from the Stage I air investigation, based on quality assurance and quality control concerns. Following discussions with EPA regarding approval of the draft Stage I Report, it was agreed that the air investigation would be repeated to augment and verify results from Stage I, and that the draft Work Plan was approved with the inclusion of the Stage II air investigation. A proposal for the Stage II air investigation, which is given in **Attachment 4**, was submitted to EPA for comment and review with the September 1 draft responses; no modifications to the proposal were requested by EPA. The proposed Stage II air investigation is included in the final Supplemental Work Plan.

In accordance with the agreement of the Hassayampa Technical Work Group, submittal of the following documents fulfills the obligations of the Respondents under Subsection VII.B.4 of the Administrative Consent Order:

1. **the draft Stage I Report, which was submitted on March 13, 1989;**

2. **the present letter, with which the draft Stage I Report is considered final; and**

3. **the final Supplemental Work Plan for Stage II of the Remedial Investigation, which is submitted herewith under separate cover.**

Although modifications to the draft Stage I Report are discussed in detail in the attached responses to comments, the following list summarizes errata for selected typographical or grammatical errors:

VOLUME I:

PAGE NO.	PARAGRAPH	MODIFICATION
5	no. 10	The phrase "in Unit B then in Unit A" should be replaced with the phrase "in Unit B than in Unit A"
15	fourth	The word "west" should be replaced with the word "east" in the third line of text from the bottom of the page.
27	first	The words "indicate that" should precede the word "several" in the third line of text from the top of the page.
27	second	The phrase "volumes reported may be representative" should be replaced with the phrase "volumes reported may not be representative".
53	fourth	The phrase "several orders of magnitude better" should be replaced with the phrase "several orders of magnitude lower".

VOLUME II:

TABLE NO.	MODIFICATION
11c	The TLV of "1,800,000" for the C6 aliphatic hydrocarbon should be replaced by the value "180,000", which is the TLV for n-hexane.
38	The number designation for the potential disposal alternative "Discharge to Sewage Effluent Pipeline" should be modified to conform to the number designation of the corresponding potential remedial alternative.

If you have questions or require further discussion, please contact us.

Very truly yours,
ERROL L. MONTGOMERY & ASSOCIATES, INC.

William R. Victor
William R. Victor

SENT VIA FEDERAL EXPRESS

Attachments (7)

cc w/attachments and enclosure:
A. T. Wilson (3)
Mason Bolitho (3)
James G. Derouin (2)
Robert J. Lloyd (2)
David P. Kimball (2)
Kim E. Williamson (2)
Charles A. Bischoff (1)
Errol L. Montgomery (1)
Ronald Frehner (1)
Carl C. Meier (1)
Kenneth G. Ford (1)
Robert W. Hacker (1)
Robert Cameron (1)
Lt. Col. John Hannah (1)
William J. Cheeseman (1)
Kevin Milliken/Charles Case (1)
G. S. Hagy (1)
Stephen H. Greene (1)
Cindy Lewis (1)
Richard C. Keiffer (1)
G. Eugene Neil (1)
Roger K. Ferland (1)
Terry A. Thompson (1)
G. Van Velsor Wolf (1)
Robert S. Kirschenbaum (1)
Richard Alpert (1)

ATTACHMENT 1a

JUL 28 1989

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
215 Fremont Street
San Francisco, Ca. 94105

25 JUL 1989

Mr. William J. Victor
Errol L. Montgomery & Associates
1075 East Fort Lowell Road, Suite B
Tucson, Arizona 85719

Dear Mr. Victor:

EPA has completed its validation of soil and groundwater data from the Remedial Investigation at the Hassayampa Landfill. This validation, in conjunction with EPA's previous review of the air sampling data, makes it possible for EPA to comment upon the draft Stage I Remedial Investigation/Feasibility Study (RI/FS) Report (hereinafter referred to as the "Stage I Report" or as the "Report") and upon the draft Supplemental Work Plan for Task F (hereinafter referred to as the "Task F Work Plan" or as the "Work Plan") with due consideration of the quality of the data collected up to this point.

The remainder of this letter is divided into the sections listed below.

I. General Discussion of Data Quality
II. Stage I Report Comments
III. Task F Work Plan Comments
IV. Summary Comments and Recommendations

Specific impacts of data quality are discussed in the Stage I Report comments and in the Task F Work Plan comments. Comments upon the two documents are grouped as general and specific comments. The recommendations on Page 7 of the Report are discussed in the Work Plan comments rather than in the Report comments.

I. General Discussion of Data Quality

Based upon the data packages reviewed, the soil and groundwater data are generally of acceptable quality. Some of the data are considered acceptable for limited purposes only; however, EPA's more serious initial concerns about the quality of the soil and groundwater data have been addressed by the supplemental information that you submitted. (I will forward a copy of the validation report in the near future.)

As you are aware, EPA still has serious concerns regarding the air sampling data. However, at this time, it does not appear that these concerns should have a drastic impact upon the continuing RI/FS.

II. Stage I Report Comments

A. General Comments:

1. Air Quality Assessment

In assessing air quality at the site, the Report relies heavily upon data from the air sampling program. But we cannot rely so heavily upon the air sampling data because of the questions that have been raised about it. At this time, however, it appears that we can at least begin to assess the air quality relying upon other information collected at the site.

In order to see elevated levels of contaminants in the air at a site such as the Hassayampa Landfill, we would generally expect to see elevated levels of those same contaminants in other media at the site. In the groundwater at the Landfill, however, we have had only isolated detections of contamination. Even in those locations, if contaminants were to partition out of the groundwater and into soil gas, the depth to groundwater still leaves a path of considerable length by which soil gas would migrate to ground surface. Soil borings have given little indication of soil contamination, although they do not account for potential levels of contaminants in the hazardous waste pits themselves. But according to the evaluation of the soil cover over the hazardous waste pits, soil gas "generated" at or above the hazardous waste pits would be slowed in its migration as it approached the surface.

Given the factors discussed above, we would not expect to find significantly elevated levels of contaminants in the air above the landfill. While methodology and data quality concerns prevent us from interpreting the air sampling data as a confirmation of this expectation, the data, at least, is not confounding. In short, statements may be made about air quality if it is also made clear that the entire database for the site is being relied upon to support such statements. Otherwise, assessments currently provided in the Report would have to be qualified (in the text of the Report itself) as being based upon somewhat questionable air sampling data.

2. Additional Data Requirements

One potentially significant missing piece of information is actual levels of contaminants in the soil gas on site. It has been EPA's experience at other sites that soil and sediment samples are not necessarily good indicators of the levels of contaminants in the soil gas. In particular, a failure to detect contaminants in soil samples has not necessarily meant that no contaminants were present in the soil gas. Soil gas concentrations would provide characterization of one more medium at the site, such that a description of ambient air quality from a partitioning perspective could be even more solidly supported.

In addition, vapor extraction has been (correctly) included on the list of remedial action technologies for evaluation in the FS. Direct soil gas measurements seem to be the most relevant data necessary to continue evaluation of vapor extraction as an appropriate technology.

B. Specific Comments:

1. Page 3, Statement #7: Because of our concerns about data quality, the portion of the last sentence on Page 3, ". . . and can safely be considered maximum values" gives too much credence to the air sampling data. The sentence should end after "quality." Note that a conforming change should be made in several other places in the document.

2. Page 4, Second Paragraph of Statement #7: This definition of "levels considered acceptable for a residential environment" needs to be qualified. Who considers it acceptable and what is its application? EPA will perform health-related comparisons as appropriate in preparing the Public Health Evaluation for the site. In any case, statements alluding to such a "definition" are also somewhat misleading when they are presented absent the accompanying risks. There is also a problem with the phrase "several orders of magnitude better." If it is meant that the levels of contaminants are lower, this should be stated. Furthermore, as discussed in the general comments above, the sampling results, due to methodology and data quality concerns, cannot be interpreted to themselves provide the confirmation stated in this paragraph. This paragraph needs major revision, although perhaps deletion would be more efficient. Again, conforming changes will be required elsewhere in the document.

3. Page 6, Statement #13: This paragraph describing the evaluation of pathways will probably require rewriting to include qualifiers based upon earlier comments, especially with respect to the air pathway. EPA's risk assessment will also include a pathway evaluation.

4. Page 15, Third Line From End of Page: Is this actually referring to the "Unidentified Pit" labeled on Figure 2 at the east end of the access road, or does it refer to another pit?

5. Table 36: As discussed above, additional data depicting soil gas contaminant concentrations are needed for further evaluation of vapor extraction in the FS. In addition, low or nondetectable soil gas levels away from the hazardous waste pits would support the notion that the source of air contaminants above background is one

or more of the pits themselves. Sufficiently high soil gas readings from directly above the pits might then indicate that improving the soil cover is warranted.

6. Table 38: The letter/number designation for "Discharge to Sewer Effluent Pipeline" is inconsistent with that for the Alternative of which it is a part in all but Alternative G3.

III. Task F Work Plan Comments

A. General Comments:

The proposed Task F may produce some interesting information, but it seems almost as likely to raise issues as to resolve them. The acceptability of the proposed activities, therefore, is largely dependent upon the level of commitment to still further investigation. At the same time, from a scheduling perspective, additional investigative iterations may not be tolerable if they are assumed to be performed consecutively as critical path events.

Viewing the Landfill on a macro scale (such that the entire hazardous waste area is considered the "source" of groundwater contamination), using the current data base and applying necessary safety factors, a groundwater extraction system could be designed to capture contamination detected at both HS-1 and MW-1UA. At this point, such a system would probably have to be designed to provide capture across the entire aquifer cross section beneath the hazardous waste portion of the Landfill, at least for Unit A. Additional water quality parameter levels might be needed for evaluation of treatment alternatives, but new monitoring wells are not necessarily required for gathering such information.

Realizing that more data should permit a degree of fine-tuning of such a groundwater remediation system, however, EPA proposes that the PRPs implement the Task F Work Plan, with certain modifications as discussed herein. One specific modification to the Work Plan would be to provide for one or more additional field work iterations to address questions raised or unanswered during Task F. To minimize potential schedule extensions, field work beyond Task F would occur as work on the FS continued. Future field work might support modifications (such as an extraction well near a more clearly delineated source of highly concentrated contaminants) to the system described in general terms above, but a macro-scale approach in the FS at this point would not generally inhibit such modifications. The FS might appropriately defer evaluation of source (soil) remedial alternatives pending additional soil borings and/or soil gas investigation.

B. Specific Comments:

1. Monitor Wells

a. Site A: Because of the relatively high levels of contamination previously found at HS-1, it would be prudent to construct the well at Site A so as to facilitate conversion of this well to an extraction well. In addition, because of the contamination found in the HS-1 borehole beneath the HS-1 well casing, it might be appropriate to install at Site A a well that is screened in Unit B.

b. Site B: The proposed Site B could potentially detect contamination from either the Special Pits Area or from Pit A. If this well site is meant to help delineate a source area, it should be placed less "ambiguously." Either directly down gradient of Pit A and further away from the Special Pits Area or somewhat further south of the proposed location (so as to be more directly down gradient of the Special Pits) are two suggested alternative locations. Because both of these pit areas represent potential sources, it may be appropriate to place wells in both of these alternative locations, rather than in one or the other. If contamination is discovered at a Site B well, is another, further up-gradient well planned to further define the lateral extent of contamination at MW-1UA?

c. Site C: Because of its distance from MW-1UA, a well at Site C may not be of much immediate use as an indicator of the lateral extent of groundwater contamination. Even if no contamination is initially detected at Site C, without intervening wells, remedial alternatives that include groundwater extraction would have to assume that contamination detected at MW-1UA is imminently approaching Site C. (In the event that a Site C well is initially uncontaminated, the future value of Site C as a down gradient "sentinel well" is acknowledged.)

c. Sites D & E: Sites D & E seem to be appropriate well locations in the event that the well at Site A detects contamination. However, these sites, or perhaps a single well site between the two but tending toward Site D, may be appropriate even if the Site A well detects nothing.

d. Figure 6: This schematic of a proposed monitor well shows horizontal slots. All previously installed monitor wells have vertical slots. Is there a reason for this change?

2. Soil Borings

Given the size and potentially variable boundaries of the hazardous waste pits, more than one slant soil boring may be needed for each pit. A failure to find contamination in only a single soil boring would not be meaningful as a general indicator of the presence or absence of contamination (or, therefore, of a source of groundwater contamination). More slant borings may be necessary, perhaps in conjunction with soil gas work.

Also, if only one slant soil boring is to be drilled at each hazardous waste pit, the placement of these borings is especially important. Every effort should be made to identify, from aerial photographs and any other historic information, the deepest and "most active" portion of each pit. The locations on Figure 2 have not been specifically justified in the text, so it is difficult to interpret just how "approximately" these locations are represented.

Why aren't any slant borings proposed for Special Pits Areas? From historical information, these areas seem to have been the most loosely managed at the Landfill. Therefore, the Special Pits should not be dismissed as potential sources of contamination.

3. Page 18, last two lines: In some sense, we cannot claim to have defined the vertical extent of groundwater contamination if we haven't defined the lateral extent.

4. Figure 2: It would be helpful to have a figure on the scale of Figure 2 that included the features that are on Figure 2 as well as the proposed monitoring well sites.

IV. Summary Comments and Recommendations

Given the nature of EPA's comments and the "interim" nature of the Stage I Report, it is conceivable that, with agreement between EPA and the PRPs as to resolution of the State's and EPA's comments, no further work may be necessary on the Stage I Report. Instead, EPA's comments could be incorporated explicitly in the RI Report itself. This strategy would preserve the resources of all of the involved parties and is particularly attractive if revising the Stage I Report might delay the overall project. Obviously, however, EPA does not intend that the net effect should be merely to postpone the discussion and resolution of substantive issues.

EPA expects that, even with the extended time that has been required to complete data validation, Task F can be completed according to the schedule indicated in the March 13, 1989 Work Plan. EPA would support the implementation of the Task F Work Plan subject to (1) a commitment to continuing the FS and performing potential follow-up field work on a parallel track and (2) agreement between the PRPs, the State and EPA with regard to certain Task F details, such as well placement. For potential value in assessing air quality, evaluating a vapor extraction remedial alternative, defining source areas and assessing the need for more effective soil cover at disposal pits, EPA also urges including soil gas work under Task F.

I will be out the week of July 31st through August 4th, but I will be available to meet during the week of August 7th to discuss these comments and any other issues regarding the Hassayampa Landfill. Please call me at 415-974-9220 if you have questions or concerns you would like to discuss before that time.

Sincerely,

Daniel D. Opalski

Daniel D. Opalski
Project Coordinator

cc: Kristie Kilgore (3)
Mason Bolitho (3)
James G. Derouin (2)
Robert J. Lloyd (2)
David P. Kimball (2)
Charles A. Bischoff
Errol L. Montgomery
Ronald Frehner
Carl C. Meier
Kenneth G. Ford
Robert W. Hacker
Robert Cameron
Lt. Col. John Hannah
William J. Cheeseman
Kevin Milliken/Charles Case
G. S. Hagy
Stephen H. Greene
Richard C. Keiffer
G. Eugene Neil
Roger K. Ferland
Terry A. Thompson
G. Van Velsor Wolf
Robert S. Kirschenbaum

ATTACHMENT 1b

RESPONSES TO COMMENTS BY
U. S. ENVIRONMENTAL PROTECTION AGENCY

The following responses are to U. S. Environmental Protection Agency (EPA) comments, dated July 25, 1989, on the draft Stage I Report and the draft Supplemental Work Plan for TASK F, both dated March 13, 1989, for the Remedial Investigation / Feasibility Study (RI/FS) for the hazardous waste area (the Site) at the Hassayampa Landfill (the landfill), Maricopa County, Arizona. Responses to comments are referenced by the sequential number of the comment and the page on which the comment is given in the EPA document. Responses were prepared by Errol L. Montgomery & Associates, Inc. (Montgomery & Associates), except where noted. Responses prepared by Conestoga-Rovers & Associates (CRA) are enclosed by brackets: [].

COMMENT I, PAGE 1 ("General Discussion of Data Quality")

Based on telephone conversations between Montgomery & Associates and EPA during the past several weeks, it is our understanding that the sole concerns of EPA for usefulness of laboratory chemical data for soil and groundwater samples were specifically regarding the gas chromatograph/mass spectrometer (GC/MS) instrument tuning data for selected soil samples analyzed for volatile organic compounds using EPA method 8240 and for selected water samples analyzed for semi-volatile organic compounds using EPA method 625. EPA has indicated verbally that these data are acceptable for "limited use". We interpret EPA's assessment to indicate that these laboratory chemical data are useful for qualitatively determining if contaminants were detected, but may not be useful for determining accurately the concentrations of compounds that are analyzed in the range of masses for which the instrument tuning data were unacceptable (please refer to our letter to EPA dated June 15, 1989). These relations indicate that EPA concurs with the conclusions given in the draft Stage I Report that volatile organic compounds were not detected in the soils samples and that semi-volatile organic compounds were not detected in the groundwater samples.

We and CRA are aware of EPA's concerns regarding the laboratory chemical data for the air investigation, and we concur that these concerns should not hinder continuance of the RI/FS.

COMMENT II.A.1, PAGE 2 ("Air Quality Assessment")

[Air monitoring data collected during Stage I provided results of air quality at the hazardous waste area of the Hassayampa Landfill. Due to quality assurance variances, it is necessary to qualify the data as estimated values as was stated in the draft Stage I Report. The values reported are considered over-estimates of Site conditions due to the nature of the Tenax cartridges to attract volatile organic compounds rather than release them. Even though the Site air quality conditions are considered to be over-estimated by the air quality data obtained, the concentrations of volatile organic compounds detected in air were low.]

[We concur that the air quality data should be interpreted with data collected from other media such as soil and groundwater. As stated by EPA, we do not expect to find significantly elevated levels of contaminants in air given the isolated detections of contamination in groundwater and the little indication of soil contamination. The only locations of significant volatile organic compound contamination are the pits themselves. Hence, the existing soil cover is effective in controlling volatile organic compound releases to air.]

[Statements made in the draft Stage I Report regarding air quality were based on the entire Site data base, although it appears that only the air monitoring data was relied upon. Future statements on air quality will reference all relevant media.]

COMMENT II.A.2, PAGES 2 AND 3 ("Additional Data Requirements")

We concur that, given the available technology for sampling soil, data obtained from laboratory chemical analyses of soil samples may not necessarily be used as a basis for conclusions regarding chemical quality of soil gas. However, CRA indicates that the collection of soil gas data is not required to complete the Risk Assessment or the Feasibility Study, including evaluation of vapor extraction as a potential remedial action. Therefore, the recommendation of such additional field investigations for the Remedial Investigation is neither technically appropriate nor cost effective.

[EPA suggests that a soil gas survey be performed based on the following four reasons:

1. **assessing air quality;**
2. **evaluating a vapor extraction remedial alternative;**
3. **defining source areas; and**
4. **assessing the need for more effective soil cover at disposal pits.]**

[CRA disputes the rationale as follows:

1. Assessing Air Quality

   [The soil gas survey would not contribute substantial information to the air quality assessment. Although it is possible to conduct theoretical estimates as to how much volatile organic compounds might be emitted to air, these estimates would be much less representative than the existing air quality measurements.]

   [Given the above, a soil gas survey is not required to assess air quality.]

2. Evaluating Soil Gas Extraction

   [A soil gas survey is not required to evaluate soil gas extraction as a remedial alternative under the Feasibility Study.]

[The majority of information required to conduct the Feasibility Study, such as the location of waste areas, the type of wastes and approximate volume of waste disposal, has already been collected. Outstanding information will be provided by Stage II.]

[Stage II will evaluate whether or not significant vertical seepage of liquid waste has occurred beneath each pit, and will evaluate the constituents which may have migrated downward.]

[In any event, a soil gas survey would provide results for only the shallow soil gas around the periphery of the pit area. The soil gas survey would not evaluate the zone of interest for a soil gas extraction system. The deeper soil gas beneath the pit area will be evaluated by scanning total organic vapors from the drill hole during the slant borings.]

3. Defining Source Areas

[The significant source areas have already been defined under Stage I. Isolated source areas, such as special pits, have been identified to fall within an area envelope which is monitored by the existing well network. In keeping with the "macro" approach, which assumes that contamination may exist anywhere within the subject area, it is unnecessary to pin point isolated sources.]

4. Assessing Soil Cover

[During Stage I, CRA/Montgomery & Associates evaluated the soil cover at Pits 1, 2, 3, and 4. This evaluation characterized the type and thickness of soil cover over each pit. During this evaluation, total organic vapors were measured while hand digging through the existing cover soil. At Pits 1, 3, and 4, total organic vapor concentrations were at the level of background concentrations with the soil cover in place, and increased to five to six parts per million at a depth of about two feet below land surface. No significant increase was noted at Pit 2. This evaluation demonstrates that the soil cover is effective and need not be further evaluated.]

COMMENT II.B.1, PAGE 3 ("Specific Comments")

[We concur that written statements on the air quality data should recognize the data qualifiers. As such, the air quality data is hereby qualified to be considered estimated values which are most likely to be overestimates of Site conditions.]

COMMENT II.B.2, PAGE 3 ("Specific Comments")

[It is recognized that EPA will be preparing the Public Health Evaluation for the Site which will provide health-related comparisons. The preliminary comparison was provided by CRA as a screening tool to demonstrate the air quality measurements were low. The comparison was prepared by CRA's toxicologist, Dr. Paul Nees, and utilizes the referenced document prepared by Rowan, Connolly, and Brown in 1984 (a copy of this reference is attached hereto as **Attachment 1c**).]

[Rowan, Connolly, and Brown (1984) prepared a comparison of air quality standards set by the American Conference of Governmental Industrial Hygienists, the Occupational Safety and Health Administration, the National Institute for Occupational Safety and Health, and the EPA. A discussion of different states' methods of modifying occupational standards to ambient air standards is also presented.]

[One of the conclusions presented by Rowan, Connolly, and Brown **(Attachment 1c)** is that "The ratios of occupational standards to long term EPA primary air standards range from five to 162." The comparative level of Threshold Limit Value (TLV) divided by 300, which is presented in the draft Stage I Report, is intended to reflect this conclusion.]

[It is recognized that the air monitoring data are qualified as estimated values. However, the volatile organic compound analysis results for air are low in comparison with the values indicated by Rowan, Connolly, and Brown **(Attachment 1c)** to approximate primary air standards. Accordingly, the use of these results in health-related comparisons is a valid preliminary screening tool.]

[The phrase "several orders of magnitude better" should read "several orders of magnitude lower".]

COMMENT II.B.3, PAGE 3 ("Specific Comments")

[As stated earlier within these responses, we concur that air quality (and the air pathway) should be reviewed in the context of contaminants absent/present in all media and their corresponding relationship. The air pathway discussion presented in the draft Stage I Report is consistent with our understanding of the entire data base. Based on this existing data, it should have been stated that the air pathway exists but the potential for human exposure is small, due to the fact that this pathway is not complete. It is recognized that EPA will be conducting a pathway assessment as part of the risk assessment.]

COMMENT II.B.4, PAGE 3 ("Specific Comments")

The word "east" should replace the word "west" in the third line of text from the bottom of page 15 of Volume I of the draft Stage I Report.

COMMENT II.B.5, PAGES 3 AND 4 ("Table 36")

Based on the responses given above for EPA comments regarding soil gas, Table 36 of Volume II of the draft Stage I Report could be changed to indicate that, although additional data are not required for the Feasibility Study to evaluate vapor extraction as a potential remedial action, the acquisition of additional data may be justified during the design stage if vapor extraction would be implemented as a remedial action.

COMMENT II.B.6, PAGE 4 ("Table 38")

The comment is correct. The number designation for the potential disposal alternative "Discharge to Sewage Effluent Pipeline" given in Table 38 of Volume II of the draft Stage I Report should be modified to conform to the designation of the corresponding potential remedial alternative.

COMMENT III.A, PAGE 4 ("Task F Work Plan - General Comments")

Concentrations of contaminants have been detected and confirmed solely in groundwater samples obtained from abandoned monitor well (C-1-5)3daa1[HS-1], located in the northeast part of the hazardous waste area, and from monitor well (C-1-5)3dab3[MW-1UA], located near the southwest part of the hazardous waste area. As stated on page 2 and pages 23 through 26 of the draft Supplemental Work Plan, the principal purpose of the proposed TASK F groundwater investigation is:

1. **to provide representative data for groundwater level and chemical quality of groundwater at proposed monitor well Site A, which is located near and in the direction of groundwater movement from abandoned monitor well (C-1-5)3daa1[HS-1];**
2. **to provide data for evaluating the lateral extent of groundwater contamination detected at monitor well MW-1UA; and**
3. **if groundwater contamination is confirmed at Site A, to provide data for evaluating the lateral extent of groundwater contamination detected at Site A.**

In addition, the proposed monitor well at Site B may provide data for evaluating the source of groundwater contamination detected at monitor well MW-1UA.

We agree that, considering the small area of the hazardous waste area and the "macro" approach to the area, sufficient groundwater data has been obtained for most purposes of the Remedial Investigation. However, because the feasibility of groundwater remedial alternatives is sensitive to the volume of contaminated groundwater in the basin-fill deposits aquifer, additional data for refinement of the general size of the zone of contaminated groundwater are required for proper evaluation of groundwater remedial alternatives.

Because the principal purpose of the TASK F groundwater investigation is to evaluate the volume of the zone of contaminated groundwater, and not to confirm potential contaminant sources, we do not presently recognize the need for groundwater investigations beyond the proposed program unless the groundwater monitoring program detects groundwater contamination in previously uncontaminated wells.

CRA indicates that sufficient data will be available after completion of the proposed work to evaluate source and/or soil remedial alternatives. Therefore, the conduct of a soil gas investigation is neither technically appropriate nor cost effective.

COMMENT III.B.1.a, PAGE 5 ("Monitor Well Site A")

For most groundwater investigations, it is neither cost effective nor appropriate to design monitor wells for potential use as extraction wells. However, based on results of the Stage I groundwater investigation, the design of the Unit A monitor wells meets the criteria for use as extraction wells for Unit A if groundwater pumping would be part of a recommended remedial action.

The small concentrations of contaminants detected in selected soil samples obtained during abandonment operations at monitor well HS-1 are not considered to be an indication that contaminated groundwater occurs in Unit B at the HS-1 site. Contaminants have not been detected and confirmed in any of the Unit B monitor wells constructed at the landfill, and groundwater contamination has not yet been confirmed at the HS-1 site by a properly constructed monitor well designed to yield representative groundwater samples from Unit A. Therefore, we believe that construction of a Unit B monitor well at the HS-1 site is neither technically appropriate nor cost effective at present.

COMMENT III.B.1.b, PAGE 5 ("Monitor Well Site B")

The principal purpose of proposed monitor well Site B is to refine the evaluation of the volume of groundwater contamination detected at monitor well MW-1UA. The location of Site B was selected based solely on distances to existing nearby monitor wells and direction of groundwater movement, and was not based on locations of known or suspected disposal pits. Identification of specific sources of groundwater contamination in the hazardous waste area would require an extensive network of groundwater monitor wells. Such a network is not justified for such a small area, particularly when a "macro" approach can address groundwater contamination more cost effectively and more appropriately.

Whether groundwater contamination is detected or not detected at Site B, the data will be used to interpolate contours of contaminant concentrations in groundwater. These contours will be used to provide estimates of the volume of contaminated groundwater for use in the Feasibility Study. Detection of groundwater contamination at Site B is not expected to be a basis for recommending additional monitor wells.

COMMENT III.B.1.c, PAGE 5 ("Monitor Well Site C")

The first preferred location for Site C is approximately half-way between the proposed Site C location and monitor well MW-1UA. However, the area between the proposed Site C location and monitor well MW-1UA is occupied by an active sanitary landfill and is not a practical area for location of a monitor well. Based on the direction of groundwater movement at the landfill, it may be possible that the zone of contaminated groundwater penetrated by monitor well MW-1UA would not necessarily be detected at monitor well (C-1-5)3dac[HS-2]. Therefore, the second preferred location for Site C is northwest from well HS-2 such that, if the zone of contaminated groundwater penetrated by monitor well MW-1UA would migrate down-gradient, it would necessarily be detected at Site C and/or well HS-2.

Although the degree of refinement of the estimated size of the zone of contaminated groundwater detected at well MW-1UA would not be greatly enhanced with the data from proposed Site C, Site C will serve as a necessary sentinel well in the direction of groundwater movement from well MW-1UA.

COMMENT III.B.1.c, PAGE 5 ("Monitor Well Sites D and E")

This comment should be numbered III.B.1.d in the EPA document. Proposed Sites D and E are properly located and both wells would be necessary to provide sufficient monitoring down-gradient from Site A and to the southeast from Site A.

COMMENT III.B.1.d, PAGE 5 ("Figure 6")

This comment should be numbered III.B.1.e in the EPA document. Four-inch diameter slotted steel casing commonly has vertically oriented slots. However, depending on the casing supplier and casing availability at the time casing is ordered, the slot orientation may be vertical or horizontal. The slot orientation shown on Figure 6 of the draft Supplementary Work Plan may or may not be representative for as-built conditions. Either slot orientation is acceptable. Vertical slots are specified in the technical specifications given in Appendix B of the comprehensive RI/FS Work Plan, dated January 29, 1988, to indicate that horizontal slots should not be special ordered if the more common vertical slots are readily available.

COMMENT III.B.2, PAGE 6 ("Soil Borings")

As stated on pages 1 and 19 of the draft Supplementary Work Plan, the purpose of the four proposed soil borings is: to provide data for chemical quality of soils beneath the principal disposal pits for hazardous waste; and to investigate the potential extent of downward migration of liquid wastes in the underlying vadose zone. The purpose is not to precisely define every potential source of vadose zone contamination; such definition would require many soil borings. The "macro" approach does not require such a high degree of source definition.

By sampling soils directly beneath the principal disposal pits, data will be obtained for investigating the types of contaminants that may have migrated downward in the vadose zone. Such data will be used in the Feasibility Study to evaluate potential remedial alternatives. In addition, soil borings drilled beneath the pits, where manifests indicate that most of the liquid wastes were disposed, will provide data for evaluating the potential extent of downward migration of wastes.

Data obtained from excavation of shallow trenches at the boundaries of the four principal pits will be used to determine the location and drilling angle for each boring. Penetration of the pits should be avoided to prevent downward displacement of wastes via drilling. At each of the pits, a single slant soil boring will be located to penetrate the vadose zone along the lengthwise dimension of the pit. The angle will be selected such that the deepest soil sample obtained from each boring will be substantially within the surface trace of the corresponding pit boundaries. Although such borings may not provide definitive conclusions regarding potential waste migration from each pit, they are expected to provide useful information for the Feasibility Study.

Based on the discussion given on pages 1 and 20 of the draft Supplementary Work Plan, it is clear that the proposed soil boring locations shown on Figure 2 of the draft Work Plan are not intended to be as-built locations and, in fact, are located on Figure 2 more to provide less crowding of information on the figure than to show exact locations.

The information obtained during Stage I indicates that the pits were relatively small excavations and were isolated from other pits to prevent the mixing of incompatible wastes. Therefore, for the purposes of the proposed soil boring investigation, additional soil borings in the Special Pits areas are not justified.

COMMENT III.B.3, PAGE 6

This comment appears to address the groundwater monitoring network for Unit B. Contaminants have not been detected and confirmed in any of the Unit B monitor wells constructed at the landfill. The existing array of Unit B monitor wells is sufficient to provide monitoring near the center of the hazardous waste area and in the direction of groundwater movement from the hazardous waste area.

COMMENT III.B.4, PAGE 6 ("Figure 2")

We will consider submitting such a figure as part of the Remedial Investigation Report, if all the features discussed in this comment can be included in a way that is not confusing.

COMMENT IV, PAGES 6 AND 7 ("Summary Comments and Recommendations")

We concur with the suggestion that the draft Stage I Report be considered "final" with the incorporation of agency comments and Respondent responses to comments.

ATTACHMENT 1c

J. ENVIRON. SCI. HEALTH, B19(7), 611-648 (1984)

EVALUATING THE USE OF OCCUPATIONAL STANDARDS FOR CONTROLLING TOXIC AIR POLLUTANTS

KEY WORDS: Toxic air pollutants, occupational health standards, air standards, air pollution

C.A. Rowan, W.M. Connolly and H.S. Brown

Office of Research and Standards
Department of Environmental Quality Engineering
One Winter Street
Boston, Massachusetts 02108

ABSTRACT

Currently, the U.S. Environmental Protection Agency has established air standards for relatively few chemicals. As a result, state agencies are faced with controlling air contaminants for a large number of chemicals posing potential public health threats. Use of occupational standards as a basis for deriving ambient air guidelines is a method used by states to control air toxics. This standard development approach is reviewed by considering the differences in the health basis and numerical values which often occur among the occupational standards set by OSHA, NIOSH and ACGIH. This study indicated that careful selection should be made of the most appropriate occupational standard to

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use to protect public health. A comparison is made of chemicals regulated by various state air toxic programs using occupational standards lowered by a safety factor to concentrations established by the U.S. EPA. It was found that the air guidelines vary, but the degree of stringency can be comparable.

INTRODUCTION

Under the Clean Air Act, the U.S. Environmental Protection Agency has the authority to establish air quality standards to protect the public's health with an ample margin of safety. Section 109 of the act covers those air pollutants for which the EPA determines that national ambient air standards are required, and since 1970, six primary ambient air standards have been set. In addition, under Section 112 of the Clean Air Act, provisions exist to establish emission standards for hazardous air pollutants. To date, only four standards have been promulgated by EPA: asbestos, beryllium, mercury, and vinyl chloride.

The lack of success in implementing regulations under Section 112 has essentially resulted in a shift of the responsibility to control toxic air emissions from the national level to individual states. State environmental agencies are so often faced with decisions regarding air emissions of unregulated and potentially toxic chemicals, that programs to regulate toxic air emissions are needed. Such determinations of need have led to air toxic programs in a number of states, including New Jersey, New York, Michigan, Texas, Kentucky, and in Philadelphia.

Numerous other states are currently proposing similar programs. Reflected in the designs of the individual state air toxics programs are the variety of methods available to set air standards for public health protection.

First, air emissions can be regulated on a chemical-by-chemical basis with specifically derived air standards. This approach while scientifically credible, is limited by the resources and time required to address numerous chemical air emissions.

Second, air emissions may be controlled by using generic guidelines allowing the opportunity to control a greater number of chemicals.

A third option includes a combination of the above approaches. A generic policy could provide a health basis for current decision-making purposes while concurrent evaluations are being made for acceptable exposure standards on individual chemicals of highest public health concern.

Given these various options and the identified needs of state agencies to control hazardous air pollutants, several states utilize a generic approach. This approach involves use of occupational standards and applying a safety margin and an averaging time.

The Massachusetts Department of Environmental Quality Engineering is currently developing an Air Toxics Program. One of the options being considered is generic guidelines. As part of that effort, we have evaluated the basis of some occupational standards and their relationship to the EPA ambient air standards and to each other.

This report consists of two sections. In part I, the scientific basis for occupational standards set by the American Conference of Governmental Industrial Hygienists (ACGIH), the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), and the Environmental Protection Agency's (EPA) air standards are compared for six chemicals. In addition, the agencies' policies for regulating airborne carcinogens are discussed. In part II, different states' methods of modifying occupational standards to ambient air standards are discussed. This paper provides a general evaluation of the technical accuracy of using occupational standards for deriving air guidelines for an air toxics program.

EVALUATION OF OCCUPATIONAL STANDARDS

In this section, occupational standards from NIOSH, OSHA, and ACGIH are examined. These standards are compared with each other and the EPA National Emission Standards for Hazardous Air Pollutants (NESHAPS), National Ambient Air Quality Standards (NAAQS), and EPA's Carcinogenic Assessment Group (CAG) data, where applicable.

Occupational standards refer to time-weighted average concentrations of airborne substances and represent conditions under which it is thought that nearly all workers may be continuously exposed on a daily basis without harmful effects. It is recognized that certain individuals may be at high risk with respect to certain substances and may experience an adverse health effect of a variable nature at levels below the standard. Furthermore, occupational standards are set for healthy adult workers, and they are not recommended to be used for general population exposures.

Techniques used in establishing occupational health guidelines may include usage of (1) environmental limits (air and/or skin exposures); (2) personal protective devices; (3) medical surveillance programs; (4) non detectable levels and reduction to ambient concentrations; (5) use permit systems; (6) best available control technology; and (7) substitution and prohibition. This multidimensional standard setting approach for worker protection significantly differs from techniques which can be used by the EPA to protect the general population.

In 1962, ACGIH began publishing the documentation from which their standards are derived (ACGIH, 1980).

ACGIH has established a TLV committee, and the members are not employed by private industry but represent complementary areas of expertise such as toxicology, engineering, industrial hygiene, analytical chemistry and medicine (Calabrese, 1978). The TLVs are recommendations for protecting worker health.

ACGIH uses the threshold limit value (TLV) designation for an 8 hour day, 40 hour week exposure period. STEL is the short term exposure limit and is generally a fifteen minute period. The ceiling for ACGIH is the concentration that should not be exceeded, even instantaneously (ACGIH, 1980).

NIOSH's function includes researching toxic effects, developing criteria, documenting the effects and recommending health standards to OSHA (Calabrese, 1978).

NIOSH recommended standards (NIOSH/OSHA, 1981) are based on a 10 hour day, 40 hour week. OSHA standards are set for an 8 hour day, 40 hour week. Both are set as time-weighted averages (TWA) (OSHA, 1978). NIOSH and OSHA utilize ceiling designations. The ceiling is generally a 15 minute exposure limit. One hour is required between successive excursions into the ceiling limit. An employee is generally allowed no more than 4 excursions per day above the ceiling limit.

Most of the OSHA standards were adopted from the 1968 ACGIH TLVs and are not based on the latest information. NIOSH has recommended to OSHA air levels for approximately 100 chemicals; however OSHA does not always adopt the recommendation. The ACGIH TLV Committee has recommended air levels for approximately 600 chemicals and OSHA has standards for a similar number.

For the same chemical, NIOSH, OSHA and ACGIH frequently set different standards. The disparity in standards often reflects varying analysis and interpretation of essentially the same data. These disparities can be seen in defining chemical carcinogens.

First, the number of substances regulated as carcinogens differ among the agencies. ACGIH has assigned TLVs for 45 carcinogens and has identified another 5 carcinogens for which TLVs are not assigned due to insufficient data on environmental conditions (ACGIH, 1982). NIOSH considers 27 chemicals as carcinogens and 4 as possible carcinogens, and recommended standards were set for all 31. OSHA has established workplace standards for 17 substances as carcinogens (NIOSH/OSHA, 1981).

Secondly, ACGIH has specified a cancer assessment procedure for chemicals based upon the available evidence, taking into account certain appropriate experimental parameters for animal data (ACGIH, 1980). In contrast to ACGIH procedures is the case-by-case approach by which NIOSH evaluates workplace carcinogens, and OSHA's attempt to categorize chemicals depending on the degree of evidence of carcinogenicity as proposed in the OSHA Cancer Policy (OSHA, 1980).

Inconsistencies in the criteria to classify carcinogens has led to differences in identifying chemical carcinogens and in worker exposure levels for these substances.

Comparison of Air Standards for Specific Chemicals

Lead

The following table illustrates the occupational standards established by the various agencies and the EPA National Ambient Air Quality Standard (NAAQS) for lead.

TABLE 1

Air Standards for Lead

OSHA	NIOSH	ACGIH	NAAQS
TWA 50ug/m^3	TWA 100ug/m^3	TLV 150ug/m^3 STEL 450ug/m^3	1.5ug/m^3 3 month average

The health basis used to derive these standards are briefly summarized below.

The National Ambient Air Quality Standard for lead of 1.5 ug/m^3 is recommended to protect children as the high risk group (U.S. EPA, 1978). To protect the high risk population EPA applied this rationale in establishing its standard.

1. Lead produces a whole spectrum of adverse health effects.
2. Elevated erythocyte protoporphyrin (EP) levels in blood is an indicator of toxicity.
3. The threshold for elevated EP in 95% of children is 15 ugPb/dl
4. Raising the ambient air level by 1 ug/m^3 leads to an increase of 2 ug/dl in blood lead level of small children (air/blood ratio of 1:2).
5. 12 ug/dl lead in children's blood is from other sources. (food, water, paints, inks, etc.). Therefore, the air cannot contribute more than 3 ug/dl.
6. Using air/blood ratio of 1:2, the ambient air standard is set at 1.5 ug/m^3.

ACGIH

The ACGIH TLV is not based upon the early biochemical changes in blood due to low level lead absorption. The TLV is based on: reports of air lead levels of 120-140 ug/m^3 for a 48-60 hour work week causing increased urinary coproporphyrin, some stippling of blood cells and anemia in workers; and two

studies where air lead levels of 200 and 300 ug/m^3 caused the body load of lead to reach the upper limit of safety, 200 ug/L in urine (ACGIH, 1980). ACGIH has indicated that certain pre-clinical physiologic effects of lead absorption (enzyme inhibition, hemoglobin decreases, altered spermatogenesis) are not disease states but physiologic adaptations (ACGIH, 1980).

NIOSH

NIOSH recommends blood lead levels to be below 60 ug/dl. This recommendation is based on the following observations (NIOSH, 1978). NIOSH examined epidemiologic studies of workers at five lead plants. The workers in every plant had high blood lead levels and symptoms of lead poisoning (hematologic, neurologic and renal damage) were also encountered. Chronic neurologic effects were demonstrated. One worker developed neuropathy after only 2 months exposure. His blood lead level was 80 ug/dl. The exposed workers developed renal impairment including abnormal glomerular filtration rates and abnormal tubular function (impaired urinary concentrating ability and reduced lead clearance).

These studies showed an increase in symptoms associated with lead intoxication and a decrease in hemoglobin concentrations as blood lead levels rose above 60 ug/dl.

A study of the General Motors plant in Muncie, Indiana which maintained an air lead level below 100 ug/m^3 in most departments indicated that over 90% of the workers had blood levels below 60 ug/dl. NIOSH concluded from this data that air lead levels below 100 ug/m^3 combined with periodic medical monitoring of workers would ensure that blood lead levels do not exceed 60 ug/dl.

OSHA

OSHA established a standard for lead at 50 ug/m^3 which is lower than the NIOSH recommended value. Although the data is limited, OSHA based its standard on three additional studies not considered by NIOSH (NIOSH/OSHA, 1981).

The OSHA standard is based on one study where 10% of the workers exposed to 50-100 ugPb/m^3 in the air developed blood lead levels above 60 ug/dl. The standard also takes into account that interruptions in enzymatic and mitochondrial subcellular processes by lead at asymptomatic levels is an impairment of health. In addition, the OSHA standard applies to reports of impairment of nerve conduction, renal function, and reproductive physiology. In regards to the latter, data indicates that blood lead levels should not exceed 30 ug/dl in prospective parents. OSHA concluded that 70% of workers exposed to 50 ug/m^3 of lead would have blood lead levels less than 40 ug/dl.

Conclusions

1. The NAAQS for lead was established to protect children who are more susceptible to lead toxicity than adults. Occupational standards, in contrast, were set for adults and are not as protective of the general population. To protect young children, EPA established that blood lead levels should be below 15 ug/dl. OSHA establishes a standard of 50 ug/m^3 air to ensure that 70% of workers will have blood lead levels below 40 ug/dl. If the occupational standards were directly applied to children, many would suffer peripheral and central nervous system effects in addition to anemia.

2. The NAAQS for lead accounts for lead exposure from nonair sources whereas occupational standards do not.

3. The adverse health effects upon which the standards are based vary (EPA and OSHA identify pre-clinical biochemical alterations at the enzymatic level). The ACGIH TLV is based on lead levels in urine. The NIOSH standard is based on blood lead levels as an indicator of clinical dysfunction (anemia and renal impairment).

4. There is a factor of 2 between the OSHA and NIOSH standards and a factor of 3 between OSHA and ACGIH. This wide divergence of values would greatly affect the degree of protection to the general population if applied to an air guideline. Comparison of EPA's NAAQS to occupational standards indicates a 33-100 fold difference.

Benzene

ACGIH cites the following evidence in support of its standard (ACGIH, 1980).

1. 60 ppm of benzene in workroom air was the lowest concentration to cause known fatal intoxication: death from aplastic anemia.

2. 90 workers exposed to 25 ppm for 13 years showed little evidence of intoxication, no dyscrasias, no leukemia.

3. Pagnotta reported few abnormalities and only one suspected leukemia at 6-25 ppm.

TABLE 2

Air Standards for Benzene

ACGIH	OSHA	NIOSH	NESHAP (Proposed)	
			Source	Emission Standard Existing Bat
TLV 10 ppm (15 min) STEL 25 ppm	TWA 10 ppm Ceiling 25 ppm	Ceiling 1 ppm (60 min)	1. Maleic Anhydride Plants	(97-99% control) New sources no emission
			2. Styrene Plants	BAT at (5 ppm)
			3. Storage Vessels	Existing (570 mg/yr) New (170 mg/yr)
			4. Fugitive Emissions	BAT at 73% control

4. No permanent injuries were reported in workers followed for 15 years at 40 ppm.

EPA

In proposing an emissions standard (NESHAP) for benzene, EPA evaluated the severity of benzene toxicity, including its hematotoxicity, causing anemia, pancytopenia, aplastic bone marrow and aplastic anemia. EPA considered the epidemiological evidence of leukemia and found a strong causal relation between acute myelogenous leukemia and benzene exposure.

For the proposed benzene NESHAP; the EPA determined that benzene emissions from existing sources with application of the best available technology (BAT) would substantially reduce the risk of leukemic deaths. The EPA also decided that the risks remaining after BAT are not unreasonable, and that in most instances no detectable benzene emissions would be allowed from new sources (U.S. EPA, 1980). BAT could reduce emissions by 73% and, with extra effort, possibly by 77%.

EPA weighed the high cost of applying these technologies against the estimated reduction in annual leukemic deaths. For example, for benzene fugitive emissions, BAT at 73% control results in estimated range of 0.05 to 0.32 excess leukemic deaths per year, and at 77% control, the estimated range is 0.04 to 0.27 excess leukemic deaths per year. The incremental health benefit from the more costly technology is a mere 0.01 to 0.05 reduction in leukemic deaths per year (U.S. EPA, 1979). The EPA decided that the risk after BAT is not unreasonable.

OSHA & NIOSH

The OSHA standard of 10 ppm TWA, had been originally adopted from the American National Standard Institute (ANSI) (ANSI, 1969). The OSHA standard is based on toxicity data available in 1969 and did not include data on carcinogenicity.

NIOSH published its original criteria document on benzene in 1974 recommending a TWA of 10 ppm. The basis of this TWA was observed hematological effects in workers at benzene concentrations of 60 ppm, and suggestive hematological changes in rubber workers at 25 ppm. In 1974, the carcinogenic properties of benzene were virtually unknown, although some studies raised the suspicion of benzene induced leukemia. Thus, NIOSH recommended further study of benzene toxicity. In 1976, NIOSH published a revised criteria document which strongly implicated benzene in producing leukemia, blood dyscrasias and chromosomal aberrations (NIOSH/1976).

In its revised recommendation document, NIOSH defined its position regarding carcinogens, that because it is not possible at present to establish a safe exposure level for a carcinogen, benzene exposure should be restricted to the lowest levels that can be measured in the workplace (NIOSH/1976). Thus NIOSH recommended a benzene ceiling concentration of 1 ppm measured over 60 minutes which was the lowest concentration detectable with 1976 technology.

OSHA sought to adopt the NIOSH standard in 1977, but after a lengthy court battle, the United States Supreme Court decided on July 2, 1980 that there was no evidence that 10 ppm was unsafe. Consequently, OSHA has not adopted the NIOSH recommendation, but maintains its original standard of 10 ppm.

Conclusions

1. Benzene is considered carcinogenic by all of the agencies; however, ACGIH specifies it as a suspect human carcinogen. The present OSHA standard is not based on carcinogenecity.
2. The ACGIH and OSHA standards are 10 times higher than the NIOSH recommended level which would greatly affect the value of a modified occupational standard for general population exposure.
3. NIOSH and EPA acknowledge that there is no known safe level of exposure to carcinogens such as benzene and recommend technology based standards. These standards differ, however, in that EPA requires facilities to apply best available control technology and NIOSH recommends limits of detection in air.

Beryllium

TABLE 3

Air Standards for Beryllium

OSHA	NIOSH	ACGIH	EPA
TWA 2 ug/m^3 Ceiling 5 ug/m^3 MAX Ceiling 25 ug/m^3 (30 min)	0.5 ug/m^3 (130 min)	TLV 2 ug/m^3	NESHAP Emission limit - 10 g/day for affected facilities and in any case so as not to exceed the ambient air level of 0.01 ug/m^3 - 30 day average

ACGIH

The ACGIH TLV Committee considered the retrospective studies of lung cancer in workers exposed to beryllium as inconclusive and cites a retrospective cohort study of nearly 4000 beryllium workers exposed from 1942 to 1967 reporting no increase in lung cancer. The TLV is based upon severe chronic lung disease, berylliosis and pneumonitis. The ACGIH Committee established a TLV of 2 ug/m^3 for beryllium noting the uncertainty as to the concentrations which cause illness and that individual cases of chronic berylliosis have occurred at concentrations close to the TLV (ACGIH, 1980).

NIOSH

In 1972, NIOSH recommended an occupational standard for beryllium of 2 ug/m^3. NIOSH has revised this standard to a concentration not to exceed 0.5 ug/m^3 for 130 minutes. The health basis includes beryllium's acute and chronic inhalation effects, skin and conjunctival damage and beryllium's carcinogenic potential (NIOSH/OSHA, 1980).

EPA

In 1973, the EPA adopted the NESHAP for beryllium limiting emissions to 10 grams/day for affected facilities with ambient air emissions not to exceed 0.01 ug/m^3 for a 30 day averaging period (U.S. EPA, 1973a). NESHAP was based on work done by the Atomic Energy Commission (AEC) which in 1949 set this 0.01 ug/m^3 beryllium air guideline to protect the ambient air of communities situated near beryllium refining companies having AEC contracts. The AEC established that the lowest concentration producing toxicity was above 0.01 ug/m^3 and less than 0.1 ug/m^3. The health basis for this level included acute and chronic pulmonary effects, and dermal and opthalmic effects attributable to beryllium exposure. Data was reviewed on the 820 cases of beryllium toxicity reported in the beryllium registry where 45 non-occupational exposures were indicated, 50% being fatal. EPA found no reports of beryllium-related illness in populations protected by the AEC's air standard and thus used the level in deriving the NESHAP.

CAG

In 1979, EPA's Carcinogen Assessment Group concluded that substantial evidence exists for beryllium carcinogenicity based on evidence from three animal species and from inconclusive human data. CAG performed a cancer risk assessment using occupational data and calculated the lifetime risk of lung cancer due to continuous exposure to beryllium at 1.0 ug/m^3 to be 27 cases per 100 people exposed (U.S. EPA, 1979).

Conclusions

1. The acceptable air level used by EPA to set the beryllium NESHAP is 50 to 200 times lower than the occupational standards.
2. Using the 1979 EPA carcinogen risk assessment it can be estimated that lifetime exposure to beryllium at ambient levels conforming to the NESHAP (0.01 ug/m^3) would result in 2.7 excess cancers per 1000 exposed individuals.
3. NIOSH and EPA's Carcinogen Assessment Group place more emphasis on the cancer evidence from animals than ACGIH and OSHA. Thus, in the case of beryllium, the occupational standard set by NIOSH is four times more stringent than ACGIH and OSHA.
4. It is important to note that the basis for the occupational standards are not always published such as in this case of the OSHA beryllium standard.

Mercury

TABLE 4

Air Standards for Mercury

OSHA	NIOSH	ACGIH	NESHAP
Hg inorganic TWA 0.1 mg/m^3 (Ceiling)	TWA 0.05 mg/m^3	TLV 0.1 mg/m^3	Emission limit 2,300 - 3,200 g/day so as not to exceed 0.001 mg/m^3 in the ambient air
Hg alkyl TWA 0.01 mg/m^3 (Ceiling) 0.04 mg/m^3		TLV 0.1 mg/m^3 STEL 0.03 mg/m^3	
Hg Vapor		TLV 0.05 mg/m^3 STEL 0.15 mg/m^3	

EPA

The EPA established emission limits based on the following:

1. Methyl mercury poisoning in the diet of Japanese resulted in genetic lesions and the poisoning of fetuses and children. EPA estimated that 30 ug/day would provide satisfactory protection against these effects.
2. Subtracting the average dietary intake (10 ug/day) from the protective level (30 ug/day) the level allowed through air absorption would be 20 ug/day.
3. 20 ug/day divided by daily inhalation capacity of 20 m^3/day results in 1.0 ug/m^3 as an ambient air guideline.

Based on this ambient air guideline, the EPA established emission limits so that the ambient air concentration of mercury would not exceed 1.0 ug/m^3 (U.S. EPA, 1973b).

ACGIH

ACGIH recommends a TLV for alkyl mercury compounds of 0.01 mg/m^3 and a STEL of 0.03 mg/m^3 based upon the severity of effects on the central nervous system and acute fatalities reported in workers at low levels. ACGIH cites a study showing no adverse effects to workers exposed to alkyl mercury compounds at concentrations of 0.01 to 0.1 mg/m^3. Noted in the health evaluation are damage to the kidney and developing fetus.

Inorganic and aryl mercury compounds have a higher TLV because very little is deposited in the central nervous system and overall toxicity is lower. The TLV for these compounds was set at 0.10 mg/m^3. Cases of tremor were observed in only 3 of 22 workers exposed to much higher concentrations than 0.1 mg/m^3. No ill effects were reported in workers exposed to inorganic and aryl mercury at less than 0.1 mg/m^3.

For mercury vapor, ACGIH recommends a TLV of 0.05 mg/m^3 and a STEL of 0.15 mg/m^3. With mercury vapor a relatively high proportion of absorbed mercury crosses the blood brain barrier and remains in the brain. In a chlorine plant, mercury vapor air concentrations were between 0.08 and 0.1 mg/m^3 of mercury and physical examination of the workers revealed no evidence of toxicity.

ACGIH acknowledges that CNS effects are less likely from mercury salts than mercury vapor. But ACGIH recognizes that renal and oral effects would be the same. Based on this, ACGIH questions the validity of the higher TLV which it established for inorganic and aryl mercury compounds (ACGIH, 1980).

OSHA

The OSHA workroom air standard for inorganic mercury is 0.1 mg/m^3. This value is a ceiling limit and is based on the American National Standards Insutitute's recommended standard (ANSI, 1971). The ANSI data included a report that no cases of mercury poisoning were found among workers exposed to less than 0.1 mg/m^3 of mercury. This study did report borderline cases of tremor in workers exposed to slightly higher levels of 0.8 mg/m^3 inorganic mercury for 20 years. For the standard, OSHA emphasizes the frequency of psychic disturbances in workers overexposed to mercury, acute toxicity resulting in renal damage, neurological and psychological impairment, and organic mercury's ability to affect the fetus if the mother is exposed during pregnancy.

NIOSH

For elemental mercury and inorganic mercury compounds NIOSH cites the same laboratory and case studies as OSHA, ACGIH and EPA and is in agreement with the reasoning and conclusions of these organizations. However, NIOSH cites two additional reports, one of toxicity occurring at concentrations of mercury between 0.01 mg/m^3 and 0.06 mg/m^3, and the other report cited concentrations of mercury between 0.005 mg/m^3 and 0.6 mg/m^3. In both reports the medical signs and symptoms included tremor, inability to concentrate, headache and mental irritability (NIOSH, 1973).

Because of these studies, NIOSH proposed a TWA of 0.05 mg/m^3 for inorganic mercury. Of interest is that NIOSH has not recommended an occupational standard for the more toxic forms of mercury, the alkyl mercury compounds.

Conclusions

1. ACGIH has a TLV and STEL for akyl mercury compounds. NIOSH has neither recommended a standard nor published a criteria document for alkyl mercury compounds. OSHA has promulgated a standard for alkyl mercury.
2. For inorganic mercury, OSHA and ACGIH are in agreement with the studies, toxicology, interpretation of data and the approximate permissible exposure limits. But OSHA is more strict in setting a ceiling of 0.1 mg/m^3, while ACGIH has a TLV of 0.1 mg/m^3.
3. NIOSH relies on two additional studies and recommends a TWA 50% lower than ACGIH for inorganic mercury.
4. The EPA considers dietary intake of mercury in formulating an acceptable ambient air level. In addition, this standard was derived from a toxicity study on methyl mercury, where ingestion, not inhalation was the route of exposure. The EPA standard is based on preventing toxicity in children whereas the occupational standards are based on adult studies.
5. The ACGIH occupational standard for inorganic mercury compounds are 100 times higher than the EPA ambient air

guideline used in setting the NESHAP. The ACGIH established a TLV for mercury vapor which is 50 times higher than the EPA basis for the NESHAP. For alkyl mercury, the OSHA and ACGIH occupational standards are 10 times higher than the EPA NESHAP basis for mercury.

Polychlorinated Biphenyls

ACGIH

For PCB-42% chlorine, ACGIH states that a TLV of 1 mg/m^3 will offer reasonably good protection against systemic intoxication. ACGIH acknowledges that this TLV of 1 mg/m^3 does not guarantee the exposed worker freedom from chloracne. ACGIH cites one study confirming mild to moderate chloracne developing in workers exposed to 0.1 mg/m^3.

For PCB-54% chlorine ACGIH established a TLV of 0.5 mg/m^3 based upon liver injury in animals and skin cancer in workers. ACGIH recommends further review of its TLVs for PCBs. ACGIH considers higher chlorinated PCB mixtures as more toxic (ACGIH, 1980).

TABLE 5

Air Standards for PCBs

	OSHA	NIOSH	ACGIH
PCB-42% chlorine	TWA 1 mg/m^3	TWA 0.001 mg/m^3	TLV 1 mg/m^3
			STEL 2 mg/m^3
PCB-54% chlorine	TWA 0.5 mg/m^3	TWA 0.001 mg/m^3	TLV 0.5 mg/m^3
			STEL 1.0 mg/m^3

NIOSH

NIOSH recommends that all PCB's be regulated as occupational carcinogens based upon reports of hepatic and pituitary tumors in animal experiments (NIOSH, 1977). NIOSH indicates the potential for reproductive effects to humans based upon animal studies. The TWA basis includes prevention from chloracne and liver injury.

Based on the above, NIOSH recommended a TWA of 0.001 mg/m^3 for total PCBs. This level represents the lowest detectable air level of PCBs by the available technology at that time.

OSHA

For PCB-42% chlorine, the OSHA TWA is based on potential liver damage, dermatitis and chloracne as human diseases caused by PCB exposure. The production of liver tumors and reproductive defects in animals following ingestion of PCB-42% chlorine was evaluated by OSHA and it was concluded that relevance to humans of these laboratory animal studies has not been established.

THE OSHA TWA for PCB-54% chlorine is based on the animal inhalation studies showing liver damage at concentrations of 1.5 mg/m^3. OSHA concluded that the liver tumors and reproductive effects demonstrated in animals was of questionable relevance to humans and the data is not used in the health basis of the standard.

OSHA also recommends liver function tests and dermatological examination and treatment for exposed workers (NIOSH/OSHA, 1981).

Conclusions

1. ACGIH and OSHA establish occupational standards 1000 times higher than NIOSH. NIOSH concluded that based upon animal data indicating reproductive and carcinogenic effects, that no safe level of PCBs can be established and recommended the lowest detectable level of PCBs in air.
2. ACGIH and OSHA health evaluations conclude that animal studies indicate a possible threshold exposure level for PCBs.
3. For chloracne, NIOSH recommends a standard low enough to protect workers, OSHA recommends periodic dermatologic examination and treatment, and ACGIH acknowledges that its PCB standard of 1.0 mg/m^3 will not insure protection from chloracne.
4. Use of an occupational standard as a basis for an ambient air standard should consider not only the extreme numerical difference among the PCB standards but the inconsistency in the health basis and its meaning to the general public. Although the NIOSH standard is more conservative, it is a technically-derived standard and its relevance to health protection questionable especially with improved analytical capabilities.

TABLE 6

Air Standards for Vinyl Chloride

OSHA	NIOSH	ACGIH	NESHAP
TWA 1 ppm ceiling 5 ppm	ceiling 1 ppm with eventual goal of zero exposure	TLV 5 ppm	BACT 5 ppm outlet concentration

Vinyl Chloride

ACGIH

ACGIH identifies vinyl chloride as a carcinogen, causing angiosarcoma in workers. Laboratory animal studies confirm vinyl chloride induced angiosarcoma, nephroblastoma and other tumors. ACGIH acknowledges the difficulty in determining an acceptable exposure limit but concludes that a TLV of 5 ppm will cause no increase in the incidence of cancer (ACGIH, 1982).

NIOSH

NIOSH identifies vinyl chloride as a carcinogen. The NIOSH ceiling of 1 ppm was set at the minimum detectable level of measurement in air. In effect, any detectable vinyl chloride is undersirable (NIOSH/OSHA, 1981).

OSHA

OSHA has not adopted the NIOSH recommended minimum detectable ceiling level transmitted to OSHA on March 11, 1974. OSHA developed its own standard based on: 1) vinyl chloride's carcinogenicity in three animal species and 2) the substantial probability that vinyl chloride has been the causal agent in cases of liver angiosarcoma (OSHA, 1974).

EPA

The EPA, through its NESHAP program, has concluded that it is difficult to determine from dose response data any safe concentration of vinyl chloride (U.S.EPA, 1975). Risk assessments show that 1 ppm vinyl chloride will cause an increase in the number of cancers in communities surrounding vinyl chloride plants. Based on these risk assessments, the EPA recommends that the best available technology be used to control outlet concentrations to 5 ppm.

Conclusions

1. Although carcinogenicity of vinyl chloride is recognized by each agency, the occupational standards differ by a factor of 5.
2. EPA is concerned with cancer induction in the general population at 1 ppm exposure levels. This level is acceptable for workers by OSHA, NIOSH and ACGIH.
3. The NIOSH occupational standard is a technology-based standard since safe levels of carcinogens cannot be determined.

COMPARISON OF METHODS TO EXTRAPOLATE OCCUPATIONAL STANDARDS TO ACCEPTABLE AMBIENT LEVELS

The U.S. EPA sets National Ambient Air Quality Standards to protect the public's health with an ample margin of safety. These ambient standards when compared with the occupational

standards, TABLES 7 and 8, illustrate the degree of difference between standards applied to the general population and the worker.

These data illustrate that occupational standards provide varying levels of protection in relation to primary air standards. With regard to the criteria pollutants having short term health effects and standards, there are almost exact correspondences between the ozone and 1-hour carbon monoxide primary air standards and occupational standards. The EPA has also proposed a one-hour ambient sulfur dioxide standard (0.75 - 1.0ppm) which also somewhat corresponds with the ACGIH (2.0ppm), NIOSH (.5ppm) and OSHA (5.0ppm) standards. Ratios of occupational standards to EPA annual standards indicate a range of 20-100/1 for nitrogen dioxide; 5.5/1 for carbon monoxide; 16.2 - 162.5/1 ✓ for sulfur dioxide; and 33 - 100/1 for lead.

Inferences can be made that (1) occupational standards provide varying levels of protection with regard to acceptable ambient air levels set by EPA; (2) occupational standards may be useful for protecting the general population against short ✓ term effects. On the other hand, although the ratio provides an indication of the differences between the standards, these chemicals are not representative of the numerous and diverse toxicological properties that many substances have, for example carcinogenicity. As a result, the ratio is of interest but presently limited in scope.

TABLE 7

Comparison of Ambient Air and Occupational Standards

	EPA NAAQS	OSHA	NIOSH	ACGIH
SO_2	80 ug/m^3, annual	13,000 ug/m^3	5000 ug/m^3*	1300 ug/m^3
	365 ug/m^3, 24 hr.			
CO	10 mg/m^3, annual	55 mg/m^3	55 mg/m3	-
	40 mg/m^3, 1 hr.	55 mg/m^3	55 mg/m^3	-
O_3	240 ug/m^3, 1 hr.	200 ug/m^3	200 ug/m^3	-
NO_2	0.05 ppm,annual	5 ppm*	3 ppm	1 ppm*
Lead	1.5 ug/m^3, 3 mo.	50 ug/m^3	100 ug/m^3	150 ug/m^3

* Ceiling value

TABLE 8

Ratio of Occupational Standard to NAAQS

	OSHA	NIOSH	ACGIH
SO_2 annual	162.5	62.5	16.2
24 hr.	35.6	13.7	3.6
CO annual	5.5	5.5	-
1 hr.	1.4	1.4	-
O_3 1 hr.	0.8	0.8	-
NO_2 annual	100.	60.	20.
Lead	33.3	66.7	100.

Use of Modified-Occupational Standards

Due to the vast numbers of chemicals that may be emitted into the air, the lack of federal guidance on many chemicals, and limited resources at the state level to develop specific air quality standards, states often use occupational standards to estimate acceptable exposures to the general public. The method generally uses the TLVs which ACGIH has set (although OSHA and NIOSH standards may be used) and reduced the standards by a conservative factor to protect sensitive groups exposed beyond a 40-hour workweek.

Using occupational standards to derive acceptable ambient air concentrations involves the designation of an averaging time for the standard. In order to compare the methods developed for various state air toxic programs, it is necessary to account for these different averaging times.

This task has recently been conducted by the Illinois EPA and will be briefly discussed (Illinois EPA, 1982). Four programs using different averaging times and factors to reduce the TLV were compared. The analysis involved calculating the relationship between maximum average concentrations expected in different averaging times in order to compare the reduction factors used. To estimate this relationship under typical conditions, an air pollution dispersion analysis was performed, and the ratios of the maximum concentrations for each averaging time to the maximum 24-hour average was calculated. This ratio allows calculation of a 24-hour equivalent TLV adjustment factor.

The following table illustrates the results of this work. Shown are the state agency's adjusted occupational standard and averaging time being used, and the 24-hour equivalent adjustment factor.

Using this comparative basis, the marked differences in stringency among the programs are apparent. For example, a 32-fold difference separates the approaches of New York and Texas. These differences result from the fact that air pollution levels averaged over a shorter time period will not reach as high a maximum value as air pollution levels averaged over longer time frames. In other words, smaller averaging times increase the stringency of the standard. Thus, the choice of the averaging time must be consistent with degree of stringency of the reduction factor applied to the occupational standard.

Table 10 demonstrates acceptable ambient air levels for four chemicals calculated according to each state's program and

TABLE 9

Comparison of Air Toxic Guidelines by Estimating the 24-hour Averaging Time Equivalent

		24-Hour Equivalent TLV Adjustment Factor
1.	Michigan TLV/100, 8 hour	1/281
2.	New York TLV/300, annual	1/17.5
3.	Texas TLV/100, 30 minute	1/561
4.	Kentucky TLV/42, 1 hour	1/235

TABLE 10

Comparison Among the Derived Ambient Air Guidelines by Four State Air Toxic Programs and U.S. EPA Air Standards

Occupational Standard	Beryllium ug/m^3	Mercury ug/m^3	Vinyl Chloride mg/m^3	Lead ug/m^3
OSHA/NIOSH/ACGIH	2.0/0.5/2.0	100*/50/10	2.0/2.0*/10.0	50/100/150
Michigan				
TLV/100 8 hour	0.02/0.005/0.02	1.0/0.5/0.1	0.02/0.02/0.1	0.5/1.0/1.5
TLV/281, 24 hour	0.007/0.002/0.007	0.4/0.2/0.04	0.007/0.007/0.04	0.2/0.4/0.53
New York				
TLV/300, annual	0.007/0.002/0.007	0.3/0.2/0.03	0.007/0.007/0.03	0.2/0.3/0.5
TLV/17.5, 24 hour	0.114**/0.028/0.114**	5.7**/3.0**/0.5	0.114/0.114/0.5	3.0**/5.7**/8.6**
Texas				
TLV/100, 30 min.	0.02/0.005/0.02	1.0/0.5/0.1	0.02/0.02/0.1	0.5/1.0/1.5
TLV/561, 24 hour	0.004/0.0009/0.004	0.2/0.09/0.02	0.004/0.004/0.02	0.09/0.2/0.27
Kentucky				
TLV/42, 1 hour	0.05/0.012/0.05	2.4**/1.2**/0.2	0.05/0.05	1.2/1.4**/3.6**
TLV/235, 24 hour	0.008/0.002/0.008	0.4/0.2/0.04	0.008/0.008/0.04	0.2/0.4/0.64
NESHAP	0.01ug/m^3,30 day ave.	1.0ug/m^3	Not specified	1.5, u g/m^3,3-mo. average (NAAQS)

* Ceiling

** May exceed NESHAP or NAAQS

using the various occupational standards. In addition, the ambient air levels of these chemicals not to be exceeded under NESHAPs or the NAAQS for lead is also listed for comparative purposes. This table clearly shows that depending upon the occupational standard chosen, derived air levels for the general public could vary significantly. The data also indicate that the modified occupational standard sometimes exceeds concentrations of air quality standards set by EPA.

CONCLUSIONS

The evaluations made in this report concerning the use of occupational standards for an air toxics program indicate the importance of choosing an appropriate dividing factor, averaging time and occupational standard. These three key aspects greatly affect the stringency of the program.

When EPA primary air standards were compared to occupational standards, it was found that the short term ambient air standards were very similar to occupational exposure levels. The data suggests that occupational standards may be suitable estimates for protecting the general population against short term exposures and effects. Concerning longer term effects, the occupational standards provide varying levels of protection with regard to acceptable ambient air standards set by EPA. The ratios of occupational standards to long term EPA primary air standards range from 5 to 162.

Even though the central focus of air standards is to prevent adverse health conditions in humans, those set for workers greatly differ from those for the general population. This is due to a number of reasons.

First of all, agency mandates are different. Occupational standards are aimed at protecting "nearly" all workers and EPA ambient air standards are established to protect the general public with a margin of safety. Whereas occupational standards are set to prevent disease in adults, namely those between 18 and 65, U.S. EPA considers persons of all ages.

The EPA standards are established by using a much broader approach to the health basis than the occupational standards. The EPA accounts for high risk groups with the reasoning that protection of the most sensitive individuals in the population will allow protection for the entire population. Occupational standards also identify and consider high risk groups, but only as they may exist in the workforce. EPA air standards are also more inclusive of health protection, because the standard setting procedure accounts for non air exposures to the chemicals.

Exposure periods for air standards are another critical difference. The EPA establishes air standards for continual exposures, that is, 24 hours a day for a lifetime. ACGIH and OSHA standards are based on 8 hours per day, 5 days a week, for a working lifetime. In contrast, NIOSH establishes recommended standards by considering a 10 hour day, forty hour work week for a working lifetime. A difference to note is the recovery time for the exposed individuals; EPA considers none, OSHA and ACGIH standards allow 16 hours between workdays and 64 hours on the weekends, and NIOSH recommended standards allow 14 hours between working days and 86 hours on weekends. Thus, depending upon the toxicological properties of a chemical, selection of the most appropriate occupational standard for extrapolation should consider these varying recovery periods.

For the several occupational standards compared, the exposure levels have been fairly similar between OSHA and ACGIH. The NIOSH recommended standards were usually, but not consistently, lower than those set by OSHA and ACGIH. Inconsistencies in the standards are influenced by a variety of factors, including different agency mandates, cancer policies, and multidimensional approaches to control exposures in workers.

Advantages of using occupational standards to derive acceptable ambient air guidelines are listed below: ✓

1. The sheer number of occupational standards greatly outnumber air standards for the general public.
2. Documentation for occupational standards has been prepared by highly qualified committees, reviewed, and are revised with new data. ✓
3. It is reasonable to assume that many of the chemicals used in the workplace may also be found in the ambient air.
4. Short term standards established by the EPA for the general public are comparable to the occupational standards. As a result, occupational standards may be ✓ fairly suitable for short term exposures to the general public.

DISCUSSION

Some state agencies, faced with the problems regarding unregulated air contaminants modify occupational standards to derive acceptable exposures to the general public. This report indicates the concerns regarding such an extrapolation procedure. One major consideration is which agency's occupational standard should be used. Often the numerical values widely differ, and the health basis is not always consistent. In order to establish valid health standards for chemicals in air, evaluations are clearly necessary when occupational standards differ among the agencies. This approach of choosing the most appropriate occupational standard offers more confidence in the air toxics program.

Choice of a safety factor to be applied to the occupational standard must account for many differences between the goal of protecting workers and the general public. Such considerations include differences in exposure periods, age, high risk groups, simultaneous exposures to ambient pollutants and recovery periods. Due to the fact that the health basis for occupational standards differ in the severity of health effects, whether a consistent safety factor should be used for irritants versus systemic toxicants should be considered.

Clearly, the stringency of the safety factor needs to be consistent with the averaging time for the standard or an ineffective control program could result.

As indicated in this report, the four state air toxic programs that were reviewed use a generic approach based on occupational standards and do so differently. This situation provides insights for state agencies that are currently developing air toxics programs.

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TRACE METAL RESIDUES IN SHELLFISH FROM MARYLAND WATERS, 1976 - 1980

KEY WORDS: Shellfish, Chesapeake Bay, trace metals, copper, zinc, lead, mercury, cadmium, chromium, arsenic, monitoring

M. Eisenberg* and J. J. Topping**

*Office of Environmental Programs, Maryland Department of Health and Mental Hygiene, 201 West Preston Street, Baltimore, Maryland 21201

**Department of Chemistry, Towson State University, Towson, Maryland 21204

ABSTRACT

Levels of seven heavy metal residues, arsenic, cadmium, chromium, copper, lead, mercury and zinc were monitored in samples of the American oyster (*Crassostrea virginica*), the soft shell clam (*Mya arenaria*), the hard shell clam (*Mercinaria mercinaria*) and the blue crab (*Callinectes sapidus*). Samples were taken from the Maryland section of the Chesapeake Bay and its tributaries over a five year period (1976-80). This study was undertaken to provide an estimate of a baseline for values of trace heavy metals. Also, the oyster,

0360-1234/84/1907-0649$3.50/0

ATTACHMENT 2a

ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

ROSE MOFFORD, GOVERNOR
RANDOLPH WOOD, DIRECTOR

JUN 12 1989

June 7, 1989
RPU89, 184

Mr. Dan Opalski, Remedial Project Manager
United States Environmental Protection Agency, Region IX
215 Fremont Street (T-4-1)
San Francisco, CA 94105

RE: Arizona Department of Environmental Quality Comments on the Hassayampa Landfill Draft Stage 1 RI/FS Report and Draft Supplemental Workplan for Task F, dated March 13, 1989

Dear Mr. Opalski:

The Arizona Department of Environmental Quality has reviewed the above referenced documents. Enclosed please find the comments regarding the documents.

As you can see, the Department has some significant concerns in regard to the documents. I apologize for the lengthy delay in forwarding the comments to you, however, the hydrologic comments required a greater length of time to compile than usual. Hopefully, the delay has not hindered the progress of the Superfund project in any way.

Thank you for the opportunity to review these documents. If you have any questions regarding the comments, please do not hesitate to contact me at (602) 257-2393.

Sincerely,

Kristie A. Kilgore

Kristie A. Kilgore
Project Manager
Remedial Projects Unit
Office of Waste Programs

cc: Bill Victor, Errol Montgomery & Associates
Mike Leach, Superfund Hydrology Unit
Lauren Evans, Remedial Projects Unit
Mason Bolitho, Department of Water Resources

Central Palm Plaza Building 2005 North Central Avenue Phoenix, Arizona 85004

ENCLOSURE
ADEQ COMMENTS

RE: DRAFT SUPPLIMENTAL WORKPLAN FOR TASK F
AND
STAGE 1 REPORT
for the
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
HAZARDOUS WASTE AREA
at
HASSAYAMPA LANDFILL
MARICOPA COUNTY, ARIZONA
dated
MARCH 13, 1989

SPECIFIC COMMENTS

STAGE 1 RI/FS REPORT

1. PAGE 3, PARAGRAPH 6

   The suggestion that liquid waste evaporated rather than percolated downwards seems unsubstantiated. Please see the general comments that follow in regard to the fate of the liquid waste.

2. PAGE 5, #10, FIRST STATEMENT

   Water in Unit A is of poorer quality with respect to which constituents? By poorer water quality, does the report mean water with high TDS?

3. PAGE 27, PARAGRAPH 1, SECOND SENTENCE

   The verb is missing from this sentence.

4. PAGE 27, PARAGRAPH 2, LAST SENTENCE

   The report implies that waste volumes were over estimated and that the potential for contaminant migration is therefore exaggerated. If so, should the last sentence read "may <u>not</u> be representative" rather than "may be representative"?

5. PAGE 50

   Was a surface water flow model used to analyze surface water flow at the site?

6. PAGE 69
   What was the measuring point for the water levels, the top-of-casing (TOC)? If so, please provide the TOC elevations.

7. PAGE 78 and 81

Several of the monitoring wells display evidence of entrapped gases. Since entrapped gases could impact the values obtained for conductivity, it may be useful to mention this possibility.

8. PAGE 92 and 93

What method was used to determine the radius of concentration circles?

GENERAL COMMENTS

1. FATE OF LIQUID WASTES UPON DISPOSAL:

Several parts of th Stage I RI/FS report mention that, due to the presence of low-permeability sediment layers (predominantly clays) which exist in the vadose zone at the base of the Upper Alluvial Deposits (UAD), any percolating liquids would tend to mound over these layers and result in a significant amount of lateral migration. However, evidence of this phenomenon was not observed in soil samples obtained from the 12 on-site soil borings. These soil samples exhibited low soil moisture contents and laboratory analysis did not detect the presence of any contaminants. The report concludes that much of the hazardous liquid must have evaporated in the diposal pits when exposed to the atmosphere or were absorbed by sediments in the vadose zone, and never reached the water table.

However, several lines of evidence indicate that liquids disposed at the site can, and in fact, have reached the water table without being detected in the vadose zone by soil borings. Sections A.1 through A.4 discuss this reasoning below:

A. Liquid Waste Evaporation:

Although there is little doubt that some evaporation of the liquid wastes did occur in the pits, the importance placed on evaportation as a cause of solvent removal from the pits is probably significantly overestimated. This is due to the fact that, although halogenated volatile organic compounds (HVOCs), the targeted contaminant for this site, are by nature prone to evaporation, a great quantity of HVOCs and a great variety of liquid wastes other than HVOCs were disposed into the pits. These include waste oils and water-diluted liquid wastes (primarily Pits #1 and #3). Since HVOCs are almost without exception more dense than both oil and water and were disposedin quantities that indicate that the solubility limits of the HVOCs were exceeded, the HVOCs would be expected to sink into the liquids and not be exposed to significant evaporation at the liquid surface.

Such a layering effect would also increase the percolation of the HVOCs into the subsurface due to the increased pressure of the overlying, less dense liquids.

B. Retention of Liquid Waste in the Vadose Zone:

Although some of the liquid waste is undoubtedly retained in the vadose zone as it percolates down, the report overestimates the degree of liquid retention. It states that a large amount of liquid retention would occur in the vadose zone, but not calculations are given which would even roughly approximate the ability of vadose zone sediments to retain liquids. A review of the lithologic descriptions of the on-site soil borings (Appendix F) indicates that the upper 25 to 40 feet of the UAD consists primarily of gravelly sands, sands, and somewhat silty sands. Percolation through such high permeability sediments would be primarily in the downward direction in response to gravity, with very little or no lateral migration (which would expose other dry soils to the liquids and possibly result in the retention of additional water in the vadose zone). In addition, sandy sediments, even those that are initially dry, retain very little moisture subsequent to saturation and internal drainage. Therefore, only small amounts of liquids could be retained in the upper, coarse-grained sections of the vadose zone and any significant storage would have to occur in the lower, fine-grained sections (primarily silts and clays) of the vadose zone.

C. Lateral Migration of Liquids in the Vadose Zone:

The report appears to exaggerate the potenial of the fine-grained sediment layers of the lower UAD to promote a significant amount of lateral migration of liquids in the vadose zone. Given a constant liquid surface source, the extent to which lateral migration of a mound will occur depends primarily upon the saturated and unsaturated properties of all sediments involved, the liquid percolation rate, the total volume of liquids available for percolation, and the antecedent soil moisture conditions in the vadose zone. Unsaturated flow of these liquids may laterally extend the effects of mounding by increasing soil moisture contents out to a certain distance as governed by capillary soil forces. However, upon reaching a maximum lateral extent, liquids within the mound (especially near the center of the mound where overlying liquid pressures would be at their highest) will move down through the low-permeability layers in response to gravity. Due to the fact that each disposal pit represents a finite quantity of liquid and because the seepage rate, q, from each disposal pit was probably not large, little lateral migration of liquids would be expected which would explain why none of the soil borings encountered soil with high moisture contents.

D. An On-Site Example:

An on-site example appears to demonstrate that migration of fluids from the pits to the groundwater is possible, and in fact, has apparently already taken place. Although this example does not involve hazardous liquid wastes, it still indicates that disposed liquids can reach groundwater and not be detected in nearby soil borings. The example derives from the hydrogeologic data obtained from two soil borings (SB-5 and SB-5) and a downgradient monitor well (MW-5UA) in the Pit A area.

Pit A was constructed simultaneously with the other disposal pits in ther hazardous waste area and began receiving liquid septic tank and cesspool wastes in 1979 or 1980. Prior to September, 1988, each of the on-site monitor wells had undergone two sampling rounds and the chemical quality of groundwater obtained from MW-5UA was typical of groundwater obtained from the monitor wells in the hazardous waste area. In the following two groundwater sampling rounds (9/13/88 and 12/5/88), however, concentrations of sodium, chloride, nitrate, and total dissolved solids (TDS) were at least twice as high as those obtained from the two original sampling events. In addition, detectable levels of phosphorous were found in the 9/13/88 sample. These chemical constituents are all inherent in domestic wastes and indicate that MW-5UA had intercepted a contaminant plume emanating from Pit A. Other explanations for this phenomenon such as incomplete well development or well purging at MW-5UA are unlikely since no other well at the site showed this dramatic increase in TDS concentrations.

Lithologic descriptions of the drill cuttings obtained from SB-4 and SB-5 (both located neat Pit A) indicate that within the lower silt and clay layers of the UAD, the soils are described as being only "slightly moist". Also, a laboratory soil moisture measurement of the silt layer situated directly above the basal clay layer of the UAD (above which is presumed that any downward migrating liquids would mound and being to migrate laterally) in SB-5 only had a soil moisture content of 18.5 percent. Silt and clay mixtures will typically have porosities ranging anywhere from 40 to 50 percent. An 18.5 percent moisture content indicates that the soil is indeed only "slightly moist" and has never been saturated since fine-grained sediments typically have very high field capacities (27 to 35 percent; Dunne and Leopold, 1978). Because moisture contents in SB-4 and SB-5 are much lower than the field capacity values and since these soils are situated too deeply to be affected by evapotranspiration, the SB-4 and SB-5 soils apparently have never been satuarated by water or liquid wastes in the vadose zone.

It is evident from the site hydrogeologic data surrounding Pit A that vertical migration of liquid wastes from Pit A to the water table can (and has) occurred without significant lateral migration of contaminants in the vadose zone.

2. **MONITOR WELL HS-1:**

Abandoned ADHS monitor well HS-1 had had the highest HVOC concentrations detected at the site. There have been different hypotheses concerning the source of the HVOCs detected in this well. The reort states that reaming operations or sloughed material from the UAD generated during drilling operations which may have been contaminated with hazardous waste could be responsible for the groundwater contamination. This is unlikely, however, since no hazardous substances were detected in soil samples obtained from the UAD in soil boring SB-6 which is located between HS-1 and Pit #3. Also, any contaminants migrating laterally in the vadose zone from Pit #1 should have been detected in SB-6 if contamination of the UAD was present at HS-1. Therefore, it appears unlikely that the groundwater contamination present in HS-1 was due to anything but predominantly vertically downward migration from a nearby contaminant source which has migrated to HS-1 by way of groundwater flow.

The argument is also made that the contamination encountered at HS-1 is not from an upgradient groundwater source, because, based on the calculated groundwater flow velocity in Unit A of 220 ft/yr, the groundwater contaminants initially detected in HS-1 in September, 1984 should have been detected in downgradient monitor wells by 1988. Laboratory analysis of four sets of groundwater samples obtained from monitor wells MW-2UA, MW-2UB, MW-4UA, and MW-4UB between April and December of 1988, indicate that no HVOCs were detected in these downgradient wells. Therefore, it is concluded that the contamination at HS-1 must have been a drilling problem and did not result from detection of a contaminant plume in the ground-water. Examination of this claim, however, indicates that groundwater velocities were calculated for geologic units A and B in using the specific yield of the aquifer in the velocity equation instead of the aquifer porosity (effective porosity).

The long-term specific yield of an aquifer consisting primarily of fine-grained sediments cannot be accurately estimated by the results of a 72 hour aquifer test. This method may be acceptable for estimating drawdowns from a pumping well,but it underestimates the correct figure for effective porosity. This is due to the fact that, in fine-grained sediments, the redistribution of water upon source removal can persist at an appreciable rate for many days and have durations of a few months (Hillel, 1971). In addition, it should be rememberd that calculations of sediment permeabilities are simply approximations and the permeability calculated for Units A and B could be higher than actual conditions. For example, utilizing a Unit A permeability only half as great as calculated, or 6 ft/day (which still may be too high for such fine-grained sediments), and an effective porosity of 0.2 (which may be too low), the groundwater velocity is about 50 feet per year. Other reasonable values could yield even lower velocities. In any case, these smaller groundwater flow velocities could account for why no HVOC contaminants have been detected as of yet in downgradient monitor wells. Regradless of the source of HVOC contamination in well HS-1, based on the presence of other monitor wells between wells MW-1UA and HS-1, and knowledge of groundwater flow directions.

Other scenarios explaining the presence of HVOCs in HS-1 might include incorrectly estimating the locations of Pits #1 and #3 and/or the fact that the clay layer, which lies directly above the basalt, appears to become much thinner in the northeast portion of the hazardous waste area and in some borings appears to be non-existent. Any liquids percolating from the base of Pit #1 or Pit#3 could mound over this clay and migrate a short distance until the clay was absent and then percolate through the basalt (basalt was mentioned as being permeable on page 24 of the report), and then directly to the water table. Such thinning of the clay layer would significantly cut down on vadose zone travel times and could explain why HVOCs were encountered at such an early date (1984) in HS-1.

3. PROPOSED SITE INVESTIGATION ACTIVITIES:

The site investigation activites proposed in Supplemental Task F Work Plan appear to focus on establishing a perimeter outside of which no HVOC groundwater contamination is present and then initiating site cleanup activities. The proposal also places a lot of emphasis upon the results of the proposed soil sampling beneath each pit (a single boring to each pit) as an adequate means of identifying contaminant sources. ADEQ is concerned that in order to effectively locate remedial devices (such as vapor extraction systems and recovery wells) a more thouough knowledge of contaminant sources and the distribution of contaminants within the vadose zone and the underlying aquifer is necessary. Upon review of both reports, it appears that this information is not known and although the proposed site investigation activites (additional soil borings and monitor wells) may add some new insight on contaminant distributions, they are insufficient and often situated in locations which are incapable of identifying contaminant sources.

a. **Soil Borings:**

The slant soil borings proposed in the Task F Work Plan attempt to identify the occurrence of any liquid contaminant migration beneath Pits #1, #2, #3, and #4. A single boring at a 10-15 degree angle from vertical would be drilled beneath each of the four pits to auger refusal. At an estimated depth of 60 feet to auger refusal (estimated depth to the top of the basalt layer) and drilling at a maximum angle of 15 degrees, the boring would have moved only 16 feet inside the perimeter of the pit. Much of the boring would only be a few feet within the pit.

Although the pits are not of great areal extent, their dimensions are large enough that a single boring, which is only going to extend a few feet into the pit interior, would not be considered representative of subsurface conditions for the entire pit. It is therefore proposed that multiple slant borings be conducted at each pit, except for Pit #2 which is small enough to warrent only a single boring. Although Pit #1 is reportedly small in size, it was designated as a disposal area for liquid organic wastes and according to the manifests received several thousand gallons of PCE and TCA. Therefore, it is a likely location to search for HVOCs in the subsurface. Also, because HVOCs have been detected in nearby monitor well HS-1, it is suggested that Pit #1 should have at least three slant borings drilled at various pit peimeter locations. At Pits #3 and #4, it is recommended that at least four slant borings be drilled due to the large size of the pits and the amount of liquid waste disposed into each (about 1.3 million gallons).

The increased number of borings is believed to be necessary, especially considering that the report claims that a majority of the contaminants have been absorbed within the soil matrix of the vadose zone.

It should be stressed, once again, that due to the very short distance that the slant borings will extend into the pit interior, even increasing the number of soil borings may not be adequate in detecting contaminant sources if percolation of liquids through the base of the pits was localized and not evenly spread over the entire Pit. In other words, the non-detection of contaminantsin the proposed borings does not exclue the pit as a potential contaminant source. Perhaps soil gas analysis could be used as a complementary technique to determine source locations.

For the slant borings, it is suggested that soil samples should be obtained at five foot intervals until auger refusal, and analyzed for the consitituents listed in the Task F Work Plan.

b.2 **Monitor Wells:**

Proposed monitor wells A through E in the Task F Work Plan, attempt to provide additional groundwater quality data in the vicinity of the two on-site wells which have detected HVOCs, MW-1UA (proposed wells B and C) and HS-1 (proposed wells A, D, and E).

Monitor well A is proposed to be completed only 10 feet from abandoned well HS-1 and shuld answer the questions surrounding the original detection of HVOCs at HS-1. In addition, optional monitor wells D and E appear to be properly located and will be useful in identifying any migration of contaminants from the HS-1 area. However, if HVOCs are detected in well A, it would be useful to install an additional monitor well (s) between well A and Pits #1 and #3 to determine the magnitude of groundwater contamination near the potential sources. It should be noted that detection of HVOCs in well A does not imply that well HS-1 is a contaminant source. A common upgradient source, such as Pit #1 or Pit #3 is far more likely.

Well C had been proposed to be located on the border of the landfill and about 700 feet to the southwest of MW-1UA for use as a downgradient monitor well to MW-1UA. Due to this great distance, the utility of this well is questionable if its purpose is to determine the donwgradient extent of the HVOC contamination detected in MW-1UA. However, if the purpose of well C is to ensure that contaminants have not migrated off-site, the well is properly located, but it should be understood that additional wells located between MW-1UA and well C might be required to delineate the downgradient extent of the HVOC plume detected at MW-1UA.

Proposed monitor well B has been tentatively positioned 280 feet upgradient of MW-1UA. A likely source for the HVOCs detected at MW-1UA are the Special Pit Areas which have been ignored by the report as a potential contaminant source during the siting of potential monitor well locations. The Special Pits received many types of liquid organic wastes, including over 7,000 gallons of TCE. Well B would be located crossgradient to the the Special Pits Areas, and if anything would be monitoring groundwater quality downgradient of Pit A (which received non-hazardous domestic waste). Well B should be located to monitor the Special Pits Areas, along with at least two other monitor wells, one of which should be positioned as a downgradient monitor well between MW-1UA and MW-2UA on the southwest corner of 1979 Special Pits Area.

KK:gh

ATTACHMENT 2b

RESPONSES TO COMMENTS BY ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

The following responses are to Arizona Department of Environmental Quality (ADEQ) comments, dated June 7, 1989, on the draft Stage I Report and the draft Supplemental Work Plan for TASK F, both dated March 13, 1989, for the Remedial Investigation / Feasibility Study (RI/FS) for the hazardous waste area (the Site) at the Hassayampa Landfill (the landfill), Maricopa County, Arizona. Responses to comments are referenced by the sequential number of the comment and the page on which the comment is given in the ADEQ document. Responses were prepared by Errol L. Montgomery & Associates, Inc. (Montgomery & Associates), except where noted. Responses prepared by Conestoga-Rovers & Associates (CRA) are enclosed by brackets: [].

SPECIFIC COMMENT 1, PAGE 1

Based on results of the Stage I investigation, on the types of waste disposed, and on the methods of disposal, there is a strong indication that substantial evaporation of the liquid wastes may have occurred. Support for this conclusion is given in the following responses to ADEQ General Comments 1, 1A, 1C, and 2.

[CRA has acquired copies of all of the Hassayampa Hazardous Waste Manifests issued for wastes over the operating life of the hazardous waste pits. These manifests are being assembled into a data base to provide a detailed evaluation of waste characteristics and volumes. CRA is evaluating the amount of evaporation which occurred from each pit by review of waste disposal and evaporation potential. By subtraction, we will be able to determine approximate volumes of volatile organic compounds which may have seeped into subsurface soil beneath each pit. These results will be given in the Feasibility Study Report.]

SPECIFIC COMMENT 2, PAGE 1

As stated in conclusion #10 on page 5 and on page 88 of Volume I of the draft Stage I Report, results for routine constituents indicate that chemical quality of groundwater is generally better in Unit B than in Unit A at the Site. Specifically, as stated on page 88, concentrations of sodium, chloride, and total dissolved solids were generally larger in groundwater samples obtained from Unit A monitor wells than in samples from Unit B monitor wells.

SPECIFIC COMMENT 3, PAGE 1

The comment is correct. The words "indicate that" should precede the word "several" in the third line of text from the top of page 27 of Volume I of the draft Stage I Report.

SPECIFIC COMMENT 4, PAGE 1

The comment is correct. The word "not" should follow the word "may" in the 15th line of text from the top of page 27 of Volume I of the draft Stage I Report.

SPECIFIC COMMENT 5, PAGE 1

A surface water flow model was not used in the Stage I investigation. Potential patterns of stormwater drainage at the hazardous waste area were assessed qualitatively by on-site visual inspection and by using surveyed altitudes of land surface. Results of this assessment are shown on Figure 20 of Volume II of the draft Stage I Report.

SPECIFIC COMMENT 6, PAGE 1

The measuring point for water levels at the monitor wells is described in Table 22, entitled "Summary of Water Level Measurements for Monitor Wells at Hassayampa Landfill, Maricopa County, Arizona", located in Volume II of the draft Stage I Report. Table 22 is cited in the text section on "Groundwater Levels and Groundwater Movement" on page 83 of Volume I of the draft Stage I Report. The measuring point is the top of the galvanized steel coupling, which is located above the sanitary well seal and on the top of the sounder access pipe. Altitude of measuring point is given in Table 22 and in Table 7, which is entitled "Summary of Topographic Survey for Monitor Wells, Exploration Boring, and Soil Borings, Hassayampa Landfill, Maricopa County, Arizona". Table 7 is given in Volume II of the draft Stage I Report and is first cited in the text section on "Results of Soil Boring Program" on page 45 of Volume I of the draft Stage I Report.

SPECIFIC COMMENT 7, PAGE 2

Substantial bubbling was observed solely in monitor wells (C-1-5)3dab1 [MW-1UB] and (C-1-5)3dab4 [MW-2UB]. As indicated on pages of 64 and 65 of Volume I of the draft Stage I Report, air bubbles were visible in the uppermost five to seven feet of the water column in the wells. Therefore, the potential affect of the air bubbles on hydraulic conductivity computed for Unit B using pumping test data is believed to be small or negligible. Because aquifer transmissivity computed using pumping test data is considered to be a "field coefficient", the practical potential affects of air bubbles on the movement of groundwater in Unit B at wells MW-1UB and MW-2UB are included in those computations.

SPECIFIC COMMENT 8, PAGE 2

Because groundwater contamination was detected and confirmed at only two monitor wells, a template was used to provide circles that would be appropriate in size for the figures on which they appear and that would show the relative difference in concentrations detected at the two wells. The sizes of the circles are proportional, as stated in the explanations for the figures.

GENERAL COMMENT 1, PAGE 2 ("Fate of Liquid Wastes Upon Disposal")

Please note that this comment from ADEQ uses much stronger language or different language than was used by Montgomery & Associates in the draft Stage I Report, and may be misleading to the casual reader. This problem is also evident in several of the subsequent comments given in the ADEQ document, but is mentioned solely in the present response.

The report conclusion referred to in this comment is given in conclusion #5 on page 3 of Volume I of the draft Stage I Report and is quoted as follows:

> "5. To provide data for evaluation of the general extent of contaminant migration from disposal pits in the vadose zone, 12 soil borings were drilled and sampled at the Site. Nine of the soil borings were located along the perimeter of the hazardous waste area; three soil borings were located in the interior of the hazardous waste area. The soil borings were drilled to auger refusal, which occurred in the upper part of the basaltic lava-flow unit. Total depth of the borings ranged from 55 to 67 feet below land surface.
>
> Results of the laboratory chemical analyses indicate that volatile organic compounds were not present in the soil samples and that no concentrations of trace metals detected exceed EP Toxicity limits.
>
> Results of laboratory geotechnical analyses of vertical hydraulic conductivity indicate that vertical hydraulic conductivity of the soil samples was small, and these conditions would be expected to retard the downward movement of liquids and to enhance lateral spread of downward percolating

> liquids. Perched water zones were not discerned during the drilling and sampling operations.
>
> Results of the soil investigation indicate that the lithologic character of the upper alluvial deposits unit is favorable for adsorption and lateral spread of potential downward percolating liquids from the hazardous waste disposal pits. Such lateral spreading in the vadose zone was not detected during the soil boring program. Results suggest that a substantial fraction of the liquids disposed in the hazardous waste pits may have been removed via evaporation, and that adsorption of liquids in the upper alluvial deposits unit may have been substantial."

The non-detection of contaminants in monitor wells located near, and in the direction of groundwater movement from, disposal Pits 1 and 3, which manifests indicate received the largest fraction of potentially mobile liquid wastes disposed, supports the conclusion that "a substantial fraction of the liquids disposed in the hazardous waste pits may have been removed via evaporation, and that adsorption of liquids in the upper alluvial deposits unit may have been substantial".

GENERAL COMMENT 1A, PAGES 2 AND 3 ("Liquid Waste Evaporation")

This comment appears to assume that the level of liquids in selected hazardous waste disposal pits was relatively constant, with no drying periods, and that a particular set of disposal events occurred. Results of the Stage I investigation do not support these assumptions.

[CRA has acquired copies of all of the Hassayampa Hazardous Waste Manifests issued for wastes over the operating life of the hazardous waste pits. These manifests are being assembled into a data base to provide a detailed evaluation of waste characteristics and volumes. CRA is evaluating the amount of evaporation which occurred from each pit by review of waste disposal and evaporation potential. By subtraction, we will be able to determine approximate volumes of volatile organic compounds which may have seeped into subsurface soil beneath each pit. These results will be given in the Feasibility Study Report.]

Disposal events were irregular and occasional drying, or partial drying, of the pits is believed to have occurred. In a mixture of oil, solvents, and water, the solvents commonly partition preferentially to the oil rather than the water. Therefore, if the oil phase would occur at the surface of the mixture, the oil would be expected to retain a fraction of the volatile organic compounds near the surface where evaporation is most effective; the impact of evaporation on solvents in the pits may have been strong.

We do not know the precise conditions under which disposal occurred. Because lateral spread of waste liquids in the vadose zone were not detected in the soil borings and because contaminants were not detected in monitor wells located near, and in the direction of groundwater movement from, disposal pits that received the largest fraction of potentially mobile liquid wastes, a logical conclusion is that "a substantial fraction of the liquids disposed in the hazardous waste pits may have been removed via evaporation, and that adsorption of liquids in the upper alluvial deposits unit may have been substantial".

GENERAL COMMENT 1B, PAGE 3 ("Retention of Liquid Waste in the Vadose Zone")

The upper alluvial deposits unit consists chiefly of interbedded silty and gravelly sand, with cobbles and siltstone interbeds from land surface to an average depth of about 33 feet below land surface. In this depth interval, the silt content of several layers of sediment is 30 or more percent. These deposits are typical for basin-fill deposits in the Salt River Valley, in which silt and clay comprise an important fraction of the matrix material of sand and gravel deposits. Silt and clay content as low as 10 percent may result in an order of magnitude difference between vertical and horizontal hydraulic conductivity of sand and gravel deposits. Such a difference between vertical and horizontal hydraulic conductivity would be expected to enhance lateral migration of downward percolating aqueous liquids. In addition, the specific retention for layers containing substantial quantities of silt and/or clay in this depth interval would be expected to be larger than that of sand and gravel, and would be expected to retain more moisture against gravity drainage.

GENERAL COMMENT 1C, PAGE 3 ("Lateral Migration of Liquids in Vadose Zone")

The upper alluvial deposits unit consists chiefly of interbedded clayey silt, silty clay, and sandy silt, with siltstone and claystone interbeds, in the average depth interval from 33 to 57 feet. Results of laboratory geotechnical analyses of vertical hydraulic conductivity for soil samples obtained from eight soil borings in this part of the upper alluvial deposits unit indicate that vertical hydraulic conductivity of the soil samples was small, ranging from less than 1×10^{-8} centimeters per second (cm/sec) to 4.8×10^{-6} cm/sec. These conditions would be expected to strongly retard the downward movement of liquids and to strongly enhance lateral spread of downward percolating liquids.

Except for the first and last sentence of this comment, we concur with the statements made in this comment. Because lateral spread of waste liquids in the vadose zone were not detected in the soil borings and because contaminants were not detected in monitor wells located near, and in the direction of groundwater movement from, disposal pits that received the largest percentage of potentially mobile liquid wastes, a logical conclusion is that "a substantial fraction of the liquids disposed in the hazardous waste pits may have been removed via evaporation, and that adsorption of liquids in the upper alluvial deposits unit may have been substantial".

GENERAL COMMENT 1D, PAGES 4 AND 5 ("An On-Site Example")

The draft Stage I Report does not indicate or imply that it is impossible that disposed liquids could have migrated downward to groundwater without being detected in the soil borings. However, several results from the Stage I investigation indicate that a substantial fraction of the liquids disposed in the hazardous waste pits may have been removed via evaporation, and that adsorption of liquids in the upper alluvial deposits unit may have been substantial. The presentation of an example given by ADEQ in this comment is open to interpretation and is problematic. Nevertheless, it is important to note that the Respondents have committed to investigation of the impact of manifested hazardous wastes on the environment and are not responsible for septic tank wastes disposed at the landfill.

The example presented by ADEQ indicates that Pit A was constructed "simultaneously" with other pits in the hazardous waste area and began receiving septic tank waste in 1979 or 1980. We are not aware of records that indicate the time of construction of Pit A; however, inspection of Figures 4 and 5 in Volume II of the draft Stage I Report indicates that Pit A is not visible in the March 1976 aerial photo (Figure 4) of the landfill, but appears to be present on the August 1979 aerial photo (Figure 5). Several of the known pits in the hazardous waste area are not visible in the 1979 photo (Figure 5). These relations suggest that Pit A was constructed prior to August 1979 and prior to several of the pits in the hazardous waste area.

The soil moisture content cited in the comment for the soil sample obtained at a depth of about 50 feet from soil boring SB-5 is given in percent by weight. Using the data provided in the laboratory report prepared by Sergent, Hauskins & Beckwith, which is given in Figure F-13 of Appendix F of Volume III of the draft Stage I Report, the soil moisture content for this sample in percent by volume was about 31. Data in this laboratory report also indicate that porosity of the soil sample was about 37 percent. Based on the lithologic descriptions for soil boring SB-5 (Figure F-5, Appendix F), specific yield for this soil sample would be expected to be in the range from about five to 10 percent; specific retention would then be in the range from about 27 to 32 percent. These relations suggest that the moisture content of sediments penetrated by soil boring SB-5 in the lower part of the upper alluvial deposits unit may be near specific retention, and are not a basis for concluding that these sediments have "never" been saturated. In addition, chemical quality data can not be used to determine if the septic tank waste was encountered by soil borings SB-4 and SB-5 because the chemical constituents cited in the ADEQ example were not, and are commonly not, analyzed in soil samples. Finally, the comment incorrectly states that moisture content was measured for a soil sample from soil boring SB-4; no samples for laboratory soil moisture analyses were obtained from soil boring SB-4.

GENERAL COMMENT 2, PAGES 5 AND 6 ("Monitor Well HS-1")

The first paragraph of this comment concludes that the source of groundwater contamination detected at monitor well HS-1 was waste that migrated downward vertically from a nearby disposal pit and that this waste migrated to well HS-1 via movement with the groundwater. Inspection of Figure 15 of Volume I of the draft Stage I Report and Figure 3b of Volume II indicates that monitor wells (C-1-5)3dab5[MW-4UA] and (C-1-5)3dab6[MW-4UB] are located in the direction of groundwater movement from Pits 1 and 3, which manifests indicate received the largest fraction of potentially mobile liquid wastes disposed. These figures also show that well HS-1 is up-gradient and cross-gradient from Pits 1 and 3, and is not in the direction of groundwater movement from these pits. These relations indicate that, if wastes from Pits 1 and 3 migrated vertically downward to groundwater as concluded by ADEQ, contaminants should have been detected at well MW-4UA and would be unlikely to have been detected at well HS-1. Therefore, the logic for the ADEQ conclusion is faulty.

Regarding the second and third paragraphs for this ADEQ comment, in environmental investigations it is common to use conservative estimates for aquifer parameters when computing rate of groundwater movement to obtain conservatively large rates. Estimated specific yield was used on pages 84 and 85 of Volume I of the draft Stage I Report to provide a conservatively small estimate for effective porosity, which would tend to yield a conservatively large estimate for rate of groundwater movement. As indicated on page 80 of Volume I, the specific yield selected was based on analysis of hydrogeologic conditions encountered during the Stage I investigation, and was not based on results from the 12-hour pumping tests.

A factor that would tend to counteract use of a conservatively small effective porosity is that the hydraulic conductivity used in the equation shown on page 84 of Volume I was computed by dividing the aquifer transmissivity by the entire perforated interval below the water table. This procedure neglects the natural dispersion caused by interbedded sediments of differing hydraulic conductivity and would tend to minimize rate of groundwater movement.

Based on our experience, the rates of groundwater movement estimated in the draft Stage I Report are appropriate. Even if other less conservative assumptions and procedures would be used to estimate rate of groundwater movement, it would be difficult to explain why potential groundwater contamination that is assumed by ADEQ to have occurred in 1984 from Pits 1 and/or 3, which manifests indicate received the largest fraction of potentially mobile liquid wastes disposed, was not detected at monitor well MW-4UA in 1988. Monitor well MW-4UA is located within 50 feet from the edge of Pit 3 as shown on the January 1981 aerial photo of the landfill (Figure 6 of Volume II).

Regarding the last paragraph of this comment, the data obtained from the Stage I investigation do not support the assumed potential conditions described in this ADEQ paragraph. The locations of Pits 1 and 3 are known from inspection of an aerial photo taken on January 26, 1981; these locations are not up-gradient from well HS-1. The fine-grained part of the upper alluvial deposits unit is underlain by the basaltic lava-flow unit, and was encountered in all soil borings and monitor wells drilled during the Stage I investigation. Data obtained during the Stage I investigation and reported in the draft Stage I Report indicate that thickness of the fine-grained part of the upper alluvial deposits unit ranges from 15 to 35 feet in the Stage I borings and wells, and that the thickness generally increases from the southwest part of the hazardous waste area to the northeast boundary of the hazardous waste area. In addition, analysis of altitude of the top of the fine-grained part of the upper alluvial deposits unit indicates that the altitude generally increases from the area south of Pit 3 to the northeast boundary of the hazardous waste area. Therefore, assumptions by ADEQ regarding the character of the fine-grained part of the upper alluvial deposits unit are not valid. The conclusions given in the draft Stage I Report were based on data obtained during the Stage I investigation and on practical conservative assumptions regarding the hydrogeologic conditions encountered during the investigation.

GENERAL COMMENT 3, PAGE 6 ("Proposed Site Investigation Activities")

As stated on page 2 and pages 23 through 26 of the draft Supplemental Work Plan, the principal purpose of the proposed TASK F groundwater investigation is:

1. **to provide representative data for groundwater level and chemical quality of groundwater at proposed monitor well Site A, which is located near and in the direction of groundwater movement from abandoned monitor well (C-1-5)3daa1[HS-1];**
2. **to provide data for evaluating the lateral extent of groundwater contamination detected at monitor well MW-1UA; and**
3. **if groundwater contamination is confirmed at Site A, to provide data for evaluating the lateral extent of groundwater contamination detected at Site A.**

In addition, the proposed monitor well at Site B may provide data for evaluating the source of groundwater contamination detected at monitor well MW-1UA.

Results of the proposed soil boring operations are not emphasized as a definitive procedure for identifying potential contaminant sources, and the draft Work Plan is not intended to provide source definition. Additional monitor wells are proposed to provide the data necessary to refine estimates for the size of potential zones of contaminated groundwater. As stated on pages 1 and 19 of the draft Supplementary Work Plan, the purpose of the four proposed soil borings is: to provide data for chemical quality of soils beneath the principal disposal pits for hazardous waste; and to investigate the potential extent of downward migration of liquid wastes in the underlying vadose zone. The purpose is not to precisely define every potential source of vadose zone contamination; such definition would require many soil borings. CRA indicates that additional data beyond the proposed soil boring investigation are not required to properly evaluate vapor extraction as a potential remedial alternative.

GENERAL COMMENT 3a, PAGE 7 ("Soil Borings")

The angle of the proposed borings is not given in the draft Work Plan. As stated on page 20 of the draft Work Plan, data obtained from excavation of shallow trenches at the boundaries of the four principal pits will be used to determine the location and drilling angle for each boring. The location and angle of the soil borings will depend on pit geometry and the capabilities of the drilling equipment. The angle of the borings from vertical is likely to be larger than 10 or 15 degrees.

By sampling soils directly beneath the principal disposal pits, data will be obtained for investigating the types of contaminants that may have migrated downward in the vadose zone. Such data will be used in the Feasibility Study to evaluate potential remedial alternatives. In addition, soil borings drilled beneath the pits, where manifests indicate that most of the liquid wastes were disposed, will provide data for evaluating the potential extent of downward migration of wastes.

Data obtained from excavation of shallow trenches at the boundaries of the four principal pits will be used to determine the location and drilling angle for each boring. Penetration of the pits should be avoided to prevent potential downward displacement of wastes via drilling. At each of the pits, a single slant soil boring will be located to penetrate the vadose zone along the lengthwise dimension of the pit. The angle will be selected such that the deepest soil sample obtained from each boring will be substantially within the surface trace of the corresponding pit boundaries. Although such borings may not provide definitive conclusions regarding potential waste migration from each pit, they will provide substantial, useful, and necessary information for the Feasibility Study.

GENERAL COMMENT 3b, PAGE 8 ("Monitor Wells")

The number and location of monitor wells proposed in the draft Work Plan are appropriate to achieve the goals set forth for the TASK F groundwater investigation. Please refer to the responses given in **Attachment 1b** for similar comments by EPA. Considering the statements made in this ADEQ comment, it should be emphasized that, if contaminants are detected at the proposed Site A monitor well, these results alone should not be used to suggest that well HS-1 necessarily was or was not a source of groundwater contamination.

ATTACHMENT 3

MAY 8 1989

ARIZONA
DEPARTMENT
OF WATER
RESOURCES

Rose Mofford, Governor
N. W. Plummer
Director

15 South 15th Avenue
Phoenix, Arizona 85007

May 4, 1989

Bill Victor
Errol Montgomery & Associates
1075 East Fort Lowell Road, Suite B
Tucson, Arizona 85719

Dear Mr. Victor:

The Department of Water Resources has completed its review of the following documents:

- Stage I Report for RI/FS, Hazardous Waste Area, Hassayampa Landfill, Maricopa County, Arizona
- Supplemental Work Plan for Task F, RI/FS, Hazardous Waste Area, Hassayampa Landfill, Maricopa County, Arizona

We consider the above documents to be well written and have no comments. The Department's position on these documents is of course subject to revision depending on the outcome of EPA's data validation activities for Hassayampa.

There exists a possibility that EPA may propose changes in the RI/FS schedule for Hassayampa Landfill. The Department has informed EPA of its concurrence with potential schedule changes to expedite work at this site.

Thank you for the opportunity to review these documents. Please call Mason Bolitho of my staff at 542-1552 if you have questions or comments.

Sincerely,

Bruce S. Davis
Chief
Remedial Action Division

dg

cc: Bob Henckel, ADWR
Kristie Kilgore, ADEQ
Dan Opalski, EPA

ATTACHMENT 4

CRA
Consulting Engineers

CONESTOGA-ROVERS & ASSOCIATES LIMITED
651 Colby Drive,
Waterloo, Ontario, Canada N2V 1C2
(519) 884-0510

AUG 24 1989

August 23, 1989

Reference No. 2141

Mr. William R. Victor
Errol L. Montgomery & Associates
1075 E. Fort Lowell
Tuscon, Arizona
85719

Dear Mr. Victor:

Re: Hassayampa Landfill Remedial Investigation/Feasibility Study (RI/FS)
Proposed Air Monitoring - Stage 2, Task B

This letter responds to the agreement between the USEPA and the Hassayampa Steering Committee (HSC) to conduct air monitoring during the Stage 2 RI.

Background

Task B of the RI/FS work plan was developed to investigate the potential impacts on air quality arising from the former hazardous waste disposal site. This air monitoring study was completed during Stage 1.

The USEPA qualified the representativeness of these data, based on quality assurance and quality control concerns. These concerns were based on the fact that the analytical laboratory did not meet the required holding times for analysis and some artificial contamination may have appeared in the samples.

The HSC agreed to re-conduct the air monitoring following discussion with the USEPA regarding approval of the draft Stage 1 RI report. This proposed air monitoring program is to be conducted in a manner similar to the Stage 1 program, except that extra precautions are proposed for ensuring that artificial contaminants do not enter the sample and the laboratory will meet the holding time requirements.

Stage 2 Air Monitoring

Air monitoring will be conducted at five stations situated on the perimeter of the landfill, one station over the lined cuttings pit (AMP-B) and one station situated downwind of Pit #1 (AMP-A). Figure 1 depicts these locations. The exact location will be dependent on wind direction and site conditions at the time of sampling.

Volatile organic compounds (VOC) concentrations in air will be measured using Tenax (EPA Method T0-1) and charcoal (EPA Method T0-2) sorbent tubes. Wind speed, wind direction and temperature will be measured during the air sampling event. Barometric pressure and relative humidity data will be obtained from the National Weather Service at Sky Harbor Municipal Weather Office, Phoenix, Arizona.

One low volume air sampling pump will be placed at each sampling location. Each pump will be set approximately five to six feet above ground surface. At one of the sampling stations (AMP A on Figure 1), an additional sampling station will be used to obtain duplicate air samples. In addition to the collection of investigative and duplicate air samples, a trip blank and a field blank will be collected. The trip blank will consist of one Tenax tube and one charcoal tube and will be removed from the shipping cooler without opening the tubes. The field blank will be handled in the same manner as the sample tubes, except that no site air will be drawn through it. All samples will be prepared for shipment to the laboratory in the same manner.

Before and after each field sample is collected, the sampling pump will be calibrated using a representative sample calibration tube and sorbent media in line to assure that proper flow rates are maintained. A primary standard will be attached to the inlet of the sample calibration tube. The volume of air displaced and elapsed time will be recorded. The pre- and post-sample flow rates will be recorded for each sampling period. Concentration calculations for the sample period will be based on the average of the two flow rates.

At each sampling station, a series of two tubes comprised of 1.6 grams of Tenax in the first tube and 1 gram Tenax and 1 gram of charcoal in the backup tube. The Tenax material will be at the leading edge. The sampling pump will be operated for a duration of approximately eight hours during the day time and will be adjusted to draw a total of approximately 20 litres of air.

Additional field sampling protocols are as follows:

1) The culture tubes that contain the sorbent tubes will be marked with sample identification information. No marks will be made on the sorbent tubes.

2) Sorbent tubes will not be touched with bare hands. Disposable gloves will be used to handle the tubes.

3) After starting the sampler, the flow rate will be measured and the starting time, date and temperature will be recorded.

4) The sorbent tubes will be removed from the culture tubes immediately prior to sampling and will be returned to the respective culture tube immediately after sampling.

Analytical Laboratory

The Tenax and charcoal adsorbed samples collected according to Method T0-1 and T0-2, respectively. EPA Method 8240 will be used to analyze the materials adsorbed.

Appendix A contains Methods T0-1 and T0-2.

Summary

CRA proposes to conduct the air monitoring program according to USEPA Methods T0-1 and T0-2 and 8240 and the description contained herein.

Please contact the undersigned if you have any questions.

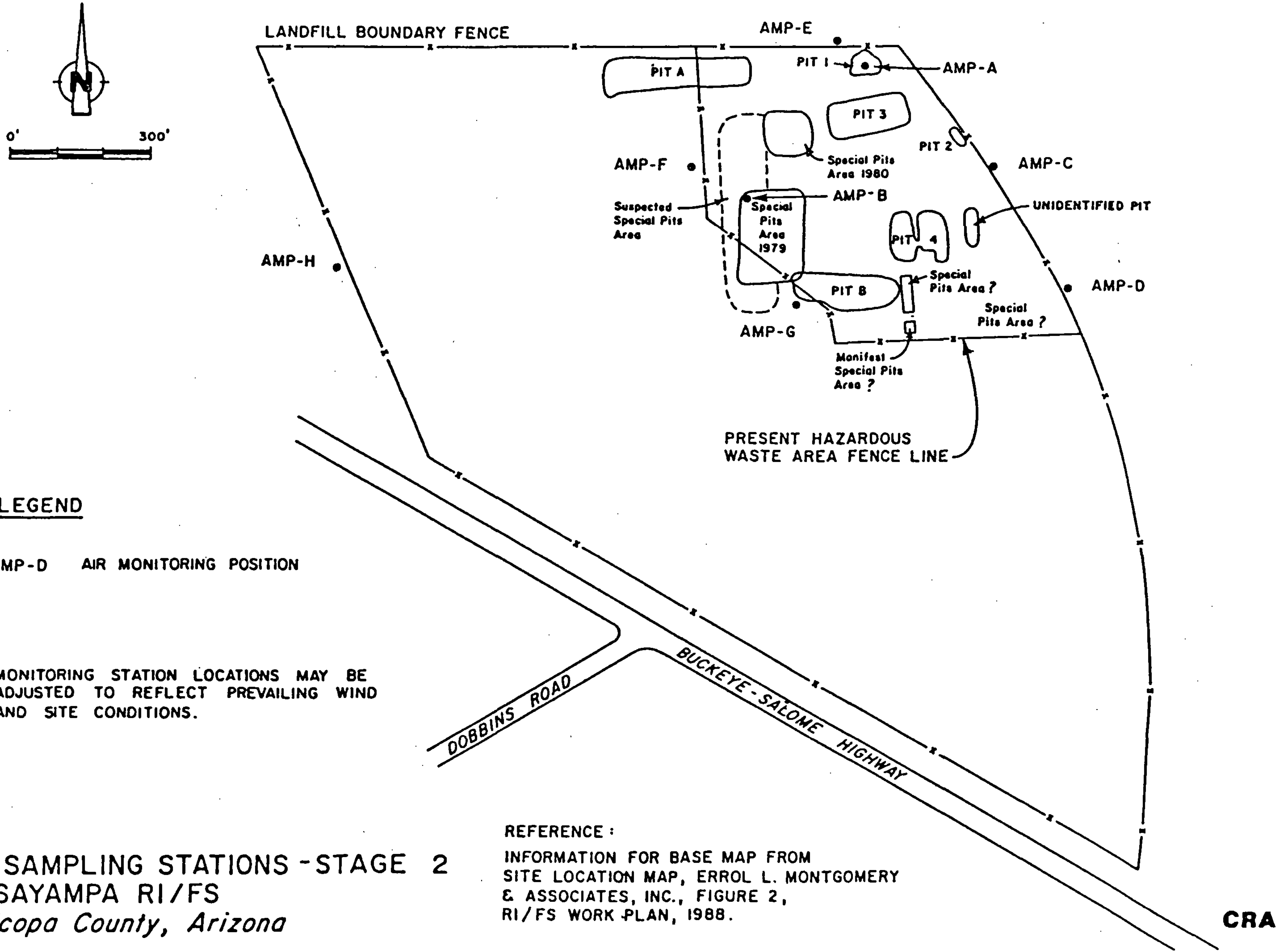
Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

Stephen M. Quigley, P. Eng.

SMQ/ec/4

c.c.: D. Haycock
R. Frehner



LEGEND

● AMP-D AIR MONITORING POSITION

NOTE: MONITORING STATION LOCATIONS MAY BE ADJUSTED TO REFLECT PREVAILING WIND AND SITE CONDITIONS.

AIR SAMPLING STATIONS - STAGE 2
HASSAYAMPA RI/FS
Maricopa County, Arizona

REFERENCE:

INFORMATION FOR BASE MAP FROM SITE LOCATION MAP, ERROL L. MONTGOMERY & ASSOCIATES, INC., FIGURE 2, RI/FS WORK PLAN, 1988.

CRA

APPENDIX A

METHODS T0-1 AND T0-2

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING [redacted]DSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC [redacted]nyl [redacted] and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2. Applicable Documents

2.1 ASTM Standards:

D1356	Definitions of Terms Related to Atmospheric Sampling and Analysis.
E355	Recommended Practice for Gas Chromatography Terms and Relationships.

2.3 Other documents:

Existing procedures (1-3).
U.S. EPA Technical Assistance Document (4).

3. Summary of Protocol

3.1 Ambient air is drawn through a cartridge containing ∿1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g. - 70°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophistacated detectors (e.g. electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Conventional air monitoring methods (e.g. for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6. INTERFERENCES

6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4 Vacuum oven - connected to water aspirator vacuum supply.

7.5 Stopwatch

7.6 Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system..

7.17 Liquid microliter syringes - 5,50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - 60 ± 5°C for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional).

8. Reagents and Materials

8.1 Empty Tenax cartridges - glass or stainless steel (See Figure 1a or b).

8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).

8.3 Glasswool - silanized.

8.4 Acetone - Pesticide quality or equivalent.

8.5 Methanol - Pesticide quality, or equivalent.

8.6 Pentane - Pesticide quality or equivalent.

8.7 Helium - Ultra pure, compressed gas. (99.9999%)

8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)

8.9 Liquid nitrogen.

8.10 Polyester gloves - for handling glass Tenax cartridges.

8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)

8.12 Perfluorotributylamine (FC-43).

8.13 Chemical Standards - Neat compounds of interest. Highest purity available.

8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9. Cartridge Construction and Preparation

9.1 Cartridge Design

9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption porcess.

Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

9.2 Tenax Purification

9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartidge preparation should be cleaned in the same manner as Tenax.

9.2.4 The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3 Cartridge Preparation and Pretreatment

9.3.1 All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2 The cartridge is packed by placing a 0.5-1cm glass-wool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3 The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4 After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g. paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge,is labeled.

9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e. no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b x W}{1.5}$$

where

V_{MAX}	is the calculated maximum total volume in liters.
V_b	is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.
W	is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} \times 1000$$

where

Q_{MAX}	is the calculated maximum flow rate in milliliters per minute.
t	is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4 The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\pi r^2}$$

where

B is the calculated linear flow velocity in centimeters per minute.
r is the internal radius of the cartridge in centimeters.

If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g. less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figures 3b shows a commercially available system based on needle valve flow controllers.

10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds four hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours.

At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g. - 20°C) before analysis if possible to maximize storage stability.

10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.

$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.

T_2 = Stop time.

T_1 = Start time.

T = Sampling time = $T_2 - T_1$, minutes

10.2.10 The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

P_A = Average barometric pressure, mmHg

t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed.

The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.1.3 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.

11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from 30°C to 200°C at 8°/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line.

11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.1.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5 x 10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standarization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g. lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria.

However, these alternate values must be repeatable on a day-to-day basis.

11.2.2 After the mass standarization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe.

The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g. 30°C). The temperature program is started at a consistent time (e.g. four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisiton is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4 If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the <u>desorb</u> mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the <u>inject</u> mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3. After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component, nanograms
A, B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.

X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.

A,B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest a linear equation ($C=0$ in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.

V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1 This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2 Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_I}{V_I} \times V_B$$

where

W_T is the total quantity of analyte to be injected into the bottle in milligrams

W_I is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms

V_I is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.

V_B is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V_T is the total volume of neat liquid to be injected in microliters.

d is the density of the neat standard in grams per milliliter.

13.1.6 The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7 To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syring warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14. Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Opreating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory:

1) assembly, calibration, and operation of the sampling system,
2) preparation, handling and storage of Tenax cartridges,
3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 Tenax Cartridge Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The assymmetry factor (See Figure 6) should be between 0.8 and 2.0. The assymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or assymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g. acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required.

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g. perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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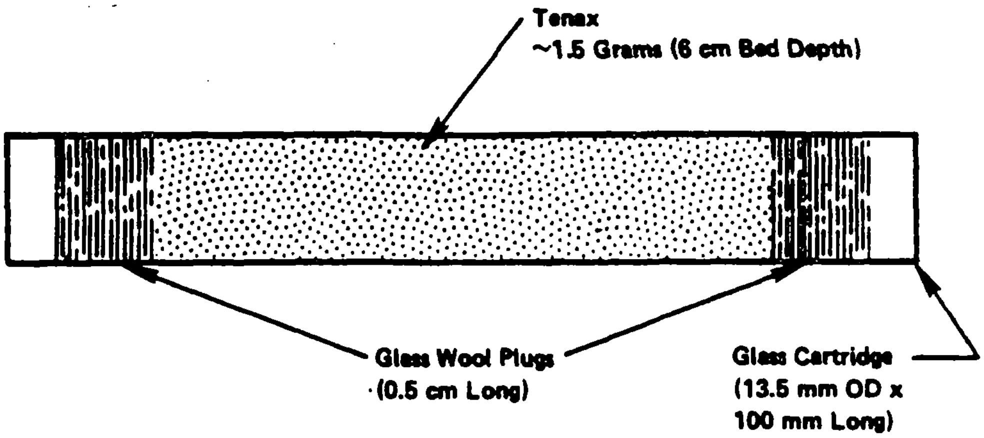
TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

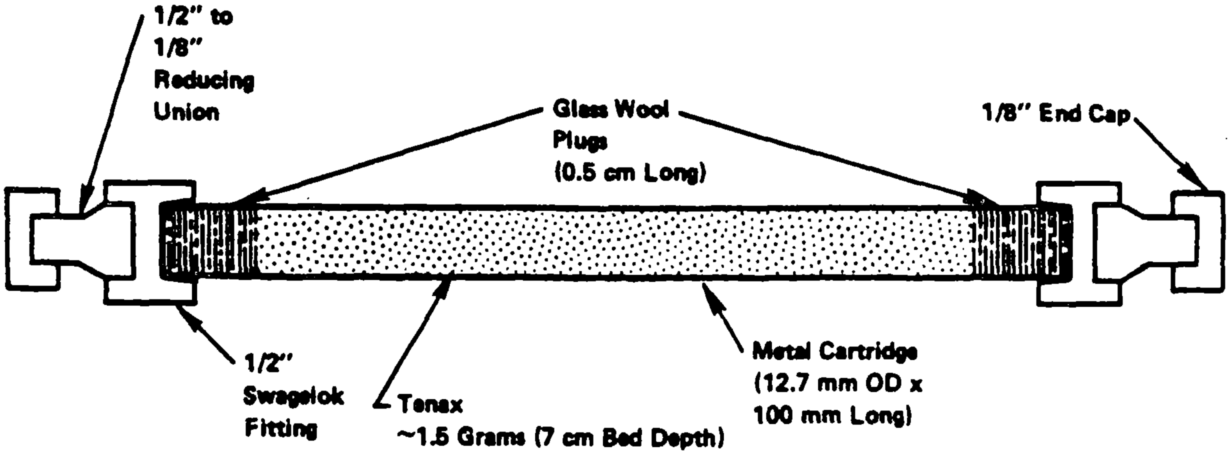
COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)-LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	∿ 200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

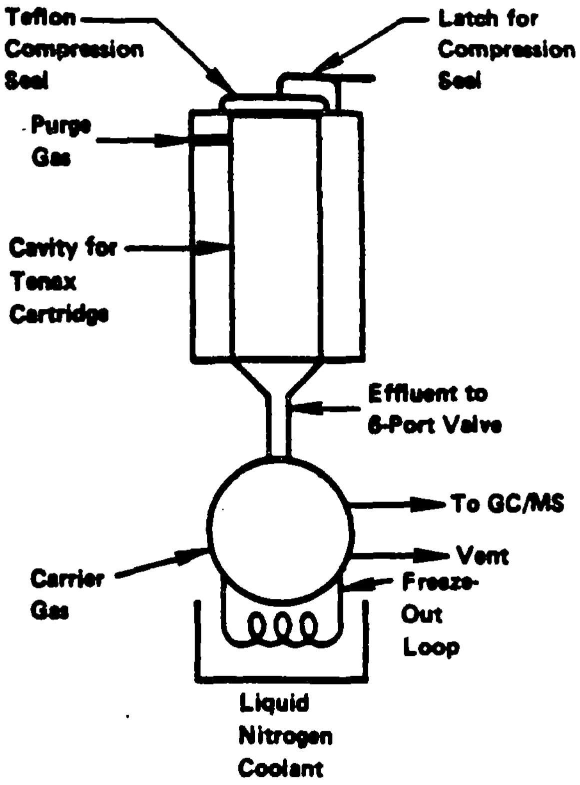


(a) Glass Cartridge

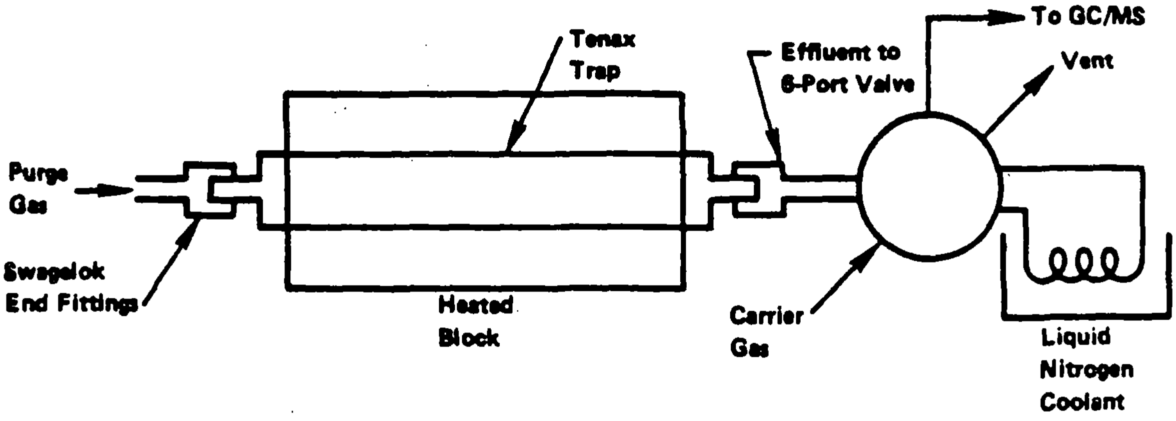


(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

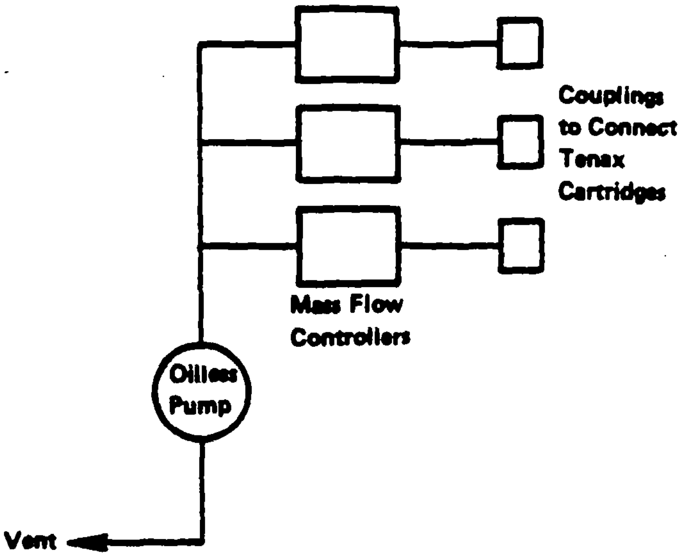


(a) Glass Cartridges (Compression Fit)

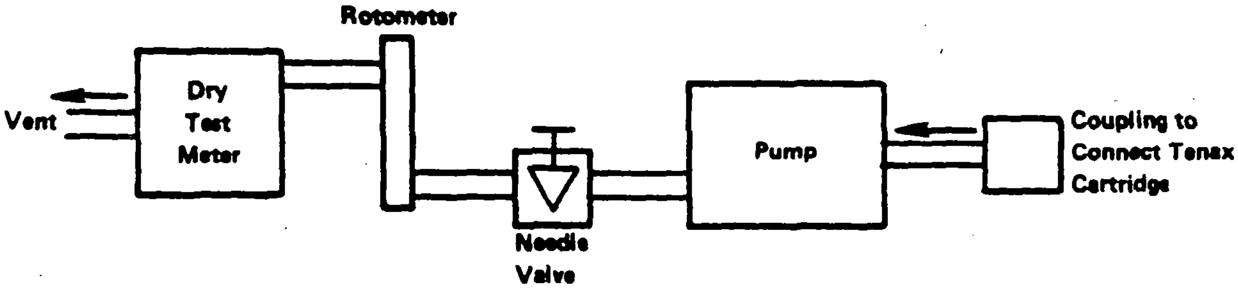


(b) Metal Cartridges (Swagelok Fittings)

FIGURE 2. TENAX CARTRIDGE DESORPTION MODULES



(a) Mass Flow Control



(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: ____________________ DATE(S) SAMPLED: ____________________

SITE: ____________________ TIME PERIOD SAMPLED: ____________________

LOCATION: ____________________ OPERATOR: ____________________

INSTRUMENT MODEL NO: ____________ CALIBRATED BY: ____________________

PUMP SERIAL NO: ____________

SAMPLING DATA

Sample Number: ____________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$= \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \underline{\qquad} \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

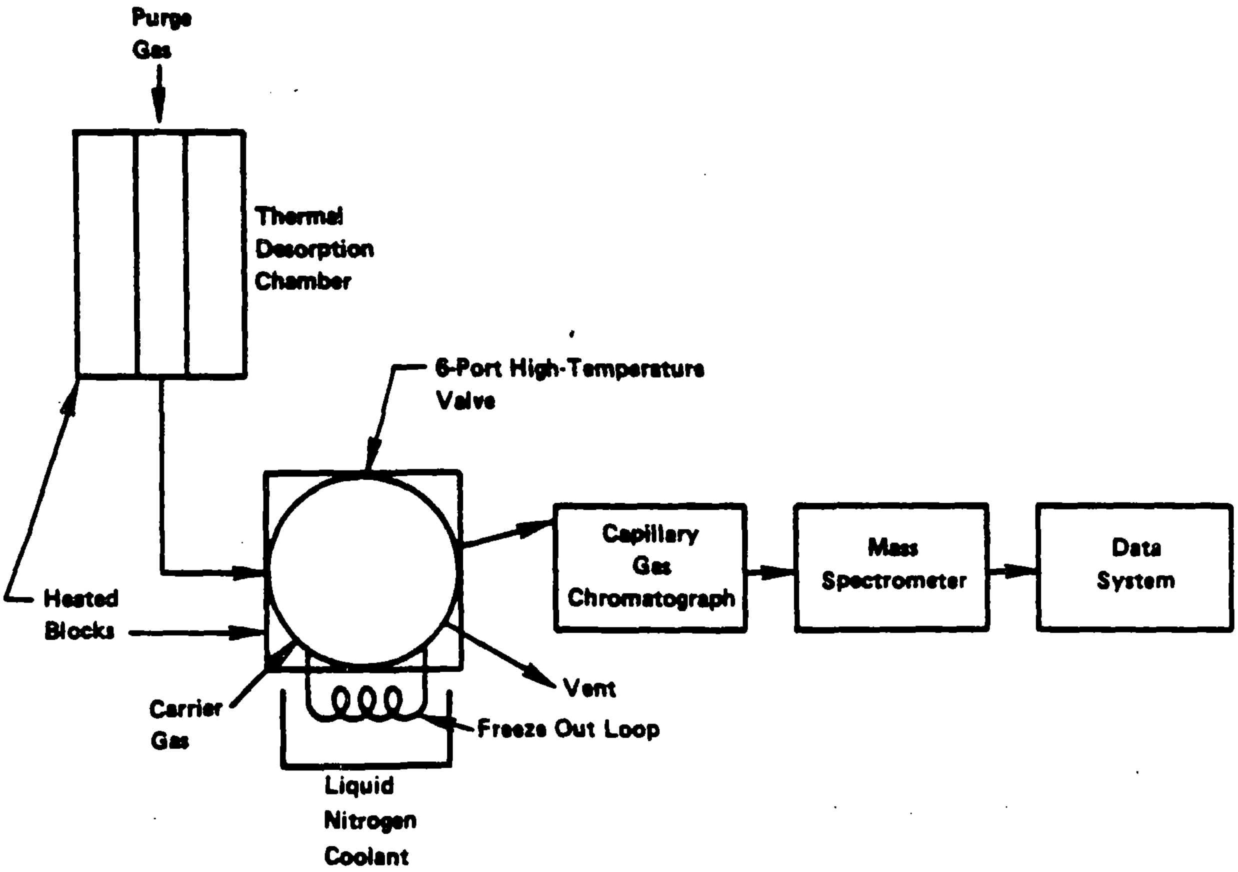
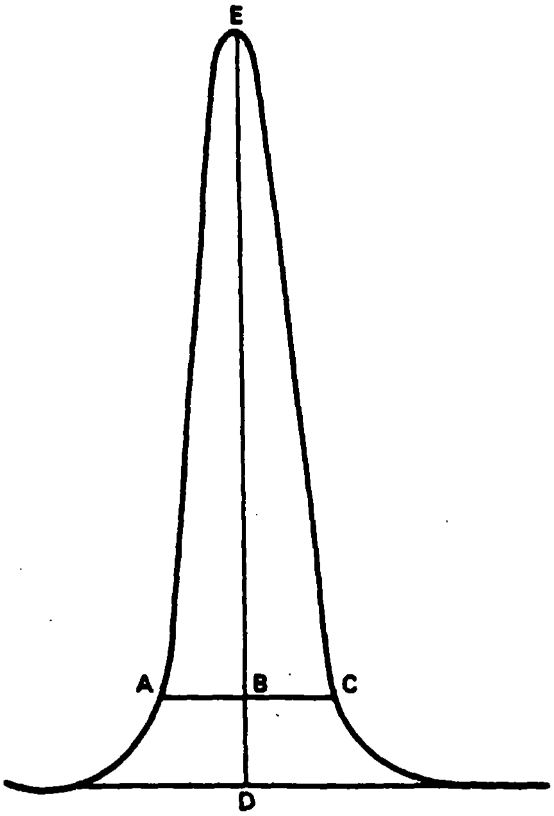


FIGURE 5. BLOCK DIAGRAM OF ANALYTICAL SYSTEM



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 6. PEAK ASYMMETRY CALCULATION

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY [redacted] MOLECULAR SIEVE ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 This document describes a procedure for collection and determination of selected volatile organic compounds which can be captured on carbon molecular sieve (CMS) adsorbents and determined by thermal desorption GC/MS techniques.

1.2 Compounds which can be determined by this method are nonpolar and nonreactive organics having boiling points in the range -15 to +120°C. However, not all compounds meeting these criteria can be determined. Compounds for which the performance of the method has been documented are listed in Table 1. The method may be extended to other compounds but additional validation by the user is required. This method has been extensively used in a single laboratory. Consequently, its general applicability has not been thoroughly documented.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E 355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.2 Other Documents

Ambient Air Studies (1,2).

U.S. EPA Technical Assistance Document (3).

3. Summary of Method

3.1 Ambient air is drawn through a cartridge containing ∿0.4 of a carbon molecular sieve (CMS) adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). After sampling, the cartridge is returned to the laboratory for analysis.

3.2 Prior to analysis the cartridge is purged with 2-3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

3.3 For analysis the cartridge is heated to 350°-400°C, under helium purge and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run.

3.4 Due to the complexity of ambient air samples, only high resolution (capillary column) GC techniques are acceptable for most applications of the method.

4. Significance

4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Many of these compounds are toxic; hence knowledge of the concentration of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Traditionally air monitoring methods for volatile organic compounds have relied on carbon adsorption followed by solvent desorption and GC analysis. Unfortunately, such methods are not sufficiently sensitive for ambient air monitoring, in most cases, because only a small portion of the sample is injected onto the GC system. Recently on-line thermal desorption methods, using organic polymeric adsorbents such as Tenax® GC, have been used for ambient air monitoring. The current method uses CMS adsorbents (e.g. Spherocarb®) to capture highly volatile organics (e.g. vinyl chloride) which are not collected on Tenax®. The use of on-line thermal desorption GC/MS yields a sensitive, specific analysis procedure.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356 (4). All abbreviations and symbols are defined with this document at the point of use.

6. Interferences

6.1 Only compounds having a mass spectrum and GC retention time similar to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.

6.2 Contamination of the CMS cartridge with the compound(s) of interest can be a problem in the method. The user must be careful in the preparation, storage, and handling of the cartridges through the entire process to minimize contamination.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - must be capable of subambient temperature programming. Unit mass resolution to 800 amu. Capable of scanning 30-300 amu region every 0.5-0.8 seconds. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Injection Unit - Designed to accommodate CMS cartridges in use (See Figure 3) and including cryogenic trap (Figure 5) and injection valve (Carle Model 5621 or equivalent).

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the CMS cartridge. (See Figure 2a or b.)

7.4 Dewar flasks - 500 mL and 5 liter.

7.5 Stopwatches.

7.6 Various pressure regulators and valves - for connecting compressed gas cylinders to GC/MS system.

7.7 Calibration gas - In aluminum cylinder. Prepared by user or vendor. For GC/MS calibration.

7.8 High pressure apparatus for preparing calibration gas cylinders (if conducted by user). Alternatively, custom prepared gas mixtures can be purchased from gas supply vendors.

7.9 Friction top can (e.g. one-gallon paint can) - With layer of activated charcoal to hold clean CMS cartridges.

7.10 Thermometer - to record ambient temperature.

7.11 Barometer (optional).

7.12 Dilution bottle - Two-liter with septum cap for standard preparation.

7.13 Teflon stirbar - 1 inch long

7.14 Gas tight syringes - 10-500 µl for standard injection onto GC/MS system and CMS cartridges.

7.15 Liquid microliter syringes - 5-50 µL for injecting neat liquid standards into dilution bottle.

7.16 Oven - 60 ± 5°C for equilibrating dilution bottle.

7.17 Magnetic stirrer.

7.18 Variable voltage transformers - (120 V and 1000 VA) and electrical connectors (or temperature controllers) to heat cartridge and cryogenic loop.

7.19 Digital pyrometer - 30 to 500°C range.

7.20 Soap bubble flow meter - 1, 10 and 100 mL calibration points.

7.21 Copper tubing (1/8 inch) and fittings for gas inlet lines.

7.22 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.23 Psychrometer (optional).

7.24 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

8. Reagents and Materials

8.1 Empty CMS cartridges - Nickel or stainless steel (See Figure 1).

8.2 CMS Adsorbent, 60/80 mesh- Spherocarb® from Analabs Inc., or equivalent.

8.3 Glasswool - silanized.

8.4 Methylene chloride - pesticide quality, or equivalent.

8.5 Gas purifier cartridge for purge and GC carrier gas containing charcoal, molecular sieves, and a drying agent. Available from various chromatography supply houses.

8.6 Helium - Ultra pure, (99.9999%) compressed gas.

8.7 Nitrogen - Ultra pure, (99.9999%) compressed gas.

8.8 Liquid nitrogen or argon (50 liter dewar).

8.9 Compressed air, if required - for operation of GC oven door.

8.10 Perfluorotributylamine (FC-43) for GC/MS calibration.

8.11 Chemical Standards - Neat compounds of interest. Highest purity available.

9. Cartridge Construction and Preparation

9.1 A suitable cartridge design in shown in Figure 1. Alternate designs have been reported (1) and are acceptable, provided the user documents their performance. The design shown in Figure 1 has a built-in heater assembly. Many users may choose to replace this heater design with a suitable separate heating block or oven to simplify the cartridge design.

9.2 The cartridge is assembled as shown in Figure 1 using standard 0.25 inch O.D. tubing (stainless steel or nickel), 1/4 inch to 1/8 inch reducing unions, 1/8 inch nuts, ferrules, and endcaps. These parts are rinsed with methylene chloride and heated at 250°C for 1 hour prior to assembly.

9.3 The thermocouple bead is fixed to the cartridge body, and insulated with a layer of Teflon tape. The heater wire (constructed from a length of thermocouple wire) is wound around the length of the cartridge and wrapped with Teflon tape to secure the wire in place. The cartridge is then wrapped with woven silica fiber insulation (Zetex or equivalent). Finally the entire assembly is wrapped with fiber glass tape.

9.4 After assembly one end of the cartridge is marked with a serial number to designate the cartridge inlet during sample collection.

9.5 The cartridges are then packed with ∿0.4 grams of CMS adsorbent. Glasswool plugs (∿0.5 inches long) are placed at each end of the cartridge to hold the adsorbent firmly in place. Care must be taken to insure that no strands of glasswool extend outside the tubing, thus causing leakage in the compression endfittings. After loading the endfittings (reducing unions and end caps) are tightened onto the cartridge.

9.6 The cartridges are conditioned for initial use by heating at 400°C overnight (at least 16 hours) with a 100 mL/minute purge of pure nitrogen. Reused cartridges need only to be heated for 4 hours and should be reanalyzed before use to ensure complete desorption of impurities.

9.7 For cartridge conditioning ultra-pure nitrogen gas is passed through a gas purifier to remove oxygen,moisture and organic contaminants. The nitrogen supply is connected to the unmarked end of the cartridge and the flow adjusted to ∿50 mL/minute using a needle valve. The gas flow from the inlet (marked) end of the cartridge is vented to the atmosphere.

9.8 The cartridge thermocouple lead is connected to a pyrometer and the heater lead is connected to a variable voltage transformer (Variac) set at 0 V. The voltage on the Variac is increased to ∿15 V and adjusted over a 3-4 minute period to stabilize the cartridge temperature at 380-400°C.

9.9 After 10-16 hours of heating (for new cartridges) the Variac is turned off and the cartridge is allowed to cool to ∿30°C, under continuing nitrogen flow.

9.10 The exit end of the cartridge is capped and then the entire cartridge is removed from the flow line and the other endcap immediately installed. The cartridges are then placed in a metal friction top (paint) can containing ∿2 inches of granulated activated charcoal (to prevent contamination of the cartridges during storage) in the bottom, beneath a retaining screen. Clean paper tissues (e.g. Kimwipes) are placed in can to avoid damage to the cartridges during shipment.

9.11 Cartridges are stored in the metal can at all times except when in use. Adhesives initially present in the cartridge insulating materials are "burnt off" during initial conditioning. Therefore, unconditioned cartridges should not be placed in the metal can since they may contaminate the other cartridges.

9.12 Cartridges are conditioned within two weeks of use. A blank from each set of cartridges is analyzed prior to use in field sampling. If an acceptable blank level is achieved, that batch of cartridges (including the cartridge serving as the blank) can be used for field sampling.

10. Sampling

10.1 Flow Rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per unit weight of adsorbent). However, all of the compounds listed in Table 1 have retention volumes (at 37°C) in excess of 100 liters/cartridge (0.4 gram CMS cartridge) except vinyl chloride for which the value is ∿30 liters/cartridge. Consequently, if vinyl chloride or similarly volatile compounds are of concern the maximum allowable sampling volume is approximately 20 liters. If such highly volatile compounds are not of concern, samples as large as 100 liters can be collected.

10.1.2 To calculate the maximum allowable sampling flow rate the following equation can be used:

$$Q_{Max} = \frac{V_{Max}}{t} \times 1000$$

where

Q_{Max} is the calculated maximum sampling rate in mL/minute.

t is the desired sampling time in minutes.

V_{Max} is the maximum allowable total volume based on the discussion in 10.1.1.

10.1.3 For the cartridge design shown in Figure 1 Q_{Max} should be between 20 and 500 mL/minute. If Q_{Max} lies outside this range the sampling time or total sampling volume must be adjusted so that this criterion is achieved.

10.1.4 The flow rate calculated in 10.1.3 defines the maximum allowable flow rate. In general, the user should collect additional samples in parallel, at successive 2- to 4-fold lower flow rates. This practice serves as a quality control procedure to check on component breakthrough and related sampling and adsorption problems, and is further discussed in the literature (5).

10.2 Sample Collection

10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow rates (e.g. less than 100 milliliters/minute). Figure 2a illustrates a sampling system based on mass flow controllers which readily allows for collection of parallel samples. Figure 2b shows a commercially available sampling system based on needle valve flow controllers.

10.2.2 Prior to sample collection the sampling flow rate is calibrated near the value used for sampling, with a "dummy" CMS cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D 3686 (4) describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.

10.2.3 The flow rate should be checked before and after each sample collection. Ideally, a rotameter or mass flow meter should be included in the sampling system to allow periodic observation of the flow rate without disrupting the sampling process.

10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process.

10.2.5 The exit (unmarked) end of the cartridge is connected to the sampling apparatus. The endcap is left on the sample inlet and the entire system is leak checked by activating the sampling pump and observing that no flow is obtained over a 1 minute period. The sampling pump is then shut off.

10.2.6 The endcap is removed from the cartridge, a particulate filter and holder are placed on the inlet end of the cartridge, and the sampling pump is started. In many situations a particulate filter is not necessary since the compounds of interest are in the vapor state. However, if, large amounts of particulate matter are encountered, the filter may be useful to prevent contamination of the cartridge. The following parameters are recorded on an appropriate data sheet (Figure 4): date, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotometer reading (if applicable), cartridge number, pump, and dry gas meter serial number.

10.2.7 The samples are collected for the desired time, periodically recording the variables listed above. At the end of the sampling period the parameters listed in 10.2.6 are recorded and the flow rate is checked. If the flows at the beginning and end of the sampling period differ by more than 10%, the cartridge should be marked as suspect.

10.2.8 The cartridges are removed (one at a time), the endcaps are replaced, and the cartridges are placed into the original container. The friction top can is sealed and packaged for immediate shipment to the analytical laboratory.

10.2.9 The average sample rate is calculated and recorded for each cartridge according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

Q_A = Average flow rate in ml/minute.
$Q_1, Q_2, \ldots Q_N$ = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.10 The total volumetric flow is obtained directly from the dry gas meter or calculated and recorded for each cartridge using the following equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

V_m = Total volume sampled in liters at measured temperature and pressure.
T = Sampling time = $T_2 - T_1$, minutes.

10.2.11 The total volume sampled (V_s) at standard conditions, 760 mm Hg and 25°C, is calculated from the following equation:

$$V_s = V_m \times \frac{Pa}{760} \times \frac{298}{273 + ta}$$

where

Pa = Average barometric pressure, mm Hg
ta = Average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Purging

11.1.1 Prior to analysis all samples are purged at room temperature with pure, dry air or nitrogen to remove water vapor. Purging is accomplished as described in 9.7 except that the gas flow is in the same direction as sample flow (i.e. marked end of cartridge is connected to the flow system).

11.1.2 The sample is purged at 500 mL/minute for 5 minutes. After purging the endcaps are immediately replaced. The cartridges are returned to the metal can or analyzed immediately.

11.1.3 If very humid air is being sampled the purge time may be increased to more efficiently remove water vapor. However, the sum of sample volume and purge volume must be less than 75% of the retention volume for the most volatile component of interest.

11.2 GC/MS Setup

11.2.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.

11.2.2 A block diagram of the analytical system required for analysis of CMS cartridges is depicted in Figure 3. The thermal desorption system must be designed to accommodate the particular cartridge configuration. For the CMS cartridge design shown in Figure 1, the cartridge heating is accomplished as described in 9.8. The use of a desorption oven, in conjunction with a simplier cartridge design is also acceptable. Exposure of the sample to metal surfaces should be minimized and only stainless steel or nickel should be employed. The volume of tubing leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.2.3 The GC column oven must be capable of being cooled to -70°C and subsequently temperature programmed to 150°C.

11.2.4 The specific GC column and temperature program employed will be dependent on the compounds of interest. Appropriate conditions are described in the literature (2). In general, a nonpolar stationary phase (e.g. SE-30, OV-1) temperature programmed from -70 to 150°C at 8°/minute will be suitable. Fused silica, bonded-phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC/MS transfer line. Fused silica columns are also more readily connected to the GC injection valve (Figure 3). A drawback of fused silica, bonded-phase columns is the lower capacity compared to coated, glass capillary columns. In most cases the column capacity will be less than 1 microgram injected for fused silica columns.

11.2.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

11.2.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 3. Helium purge flow (through the cartridge) and carrier flow are set at approximately 50 mL/minute and 2-3 mL/minute respectively. When a cartridge is not in place a union is placed in the helium purge line to ensure a continuous inert gas flow through the injection loop.

11.2.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.2.8 The MS and data system are set up according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.3. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.3 GC/MS Calibration

11.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant user prepared SOPs. Perfluorotributylamine (FC-43) should generally be employed as the reference compound. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2, as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these alternate values must be repeatable on a day-to-day basis.

11.3.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user should then calibrate the entire GC/MS system by introducing known quantities of the components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct injection of dilute vapor phase standards, prepared in a dilution bottle or compressed gas cylinder, onto the GC column, 2) injection of dilute vapor phase standards into a flowing inert gas stream directed onto a CMS cartridge, and 3) introduction of permeation or diffusion tube standards onto a CMS cartridge. Direct injection of a compressed gas cylinder (aluminum) standard containing trace levels of the compounds of interest has been found to be the most convenient practice since such standards are stable over a several month period. The standards preparation processes for the various approaches are described in Section 13. The following paragraphs describe the instrument calibration process for these approaches.

11.3.3 If the system is to be calibrated by direct injection of a vapor phase standard, the standard, in either a compressed gas cylinder or dilution flask, is obtained as described in Section 13. The MS and data system are setup for acquisition, but the ionizer filament is shut off. The GC column oven is cooled to -70°C, the injection valve is placed in the load mode, and the cryogenic loop is immersed in liquid nitrogen or liquid argon. Liquid argon is required for standards prepared in nitrogen or air, but not for standards prepared in helium. A known volume of the standard (10-1000 mL) is injected through the cryogenic loop at a rate of 10-100 mL/minute.

11.3.4 Immediately after loading the vapor phase standard, the injection valve is placed in the <u>inject</u> mode, the GC program and system clock are started, and the cryogenic loop is heated to 60°C by applying voltage (15-20 volts) to the thermocouple wire heater surrounding the loop. The voltage is adjusted to maintain a loop temperature of 60°C. An automatic temperature controller can be used in place of the manual control system. After elution of unretained components (∿3 minutes after injection) the ionizer filament is turned on and data acquisition is initiated. The helium purge line (set at 50 mL/minute) is connected to the injection valve and the valve is returned to the <u>load</u> mode. The loop temperature is <u>increased</u> to 150 °C, with helium purge, and held at this temperature until the next sample is to be loaded.

11.3.5 After the last component of interest has eluted, acquisition is terminated and the data is processed as described in Section 11.3.8. The standard injection process is repeated using different standard concentrations and/or volumes to cover the analytical range of interest.

11.3.6 If the system is to be calibrated by analysis of standard CMS cartridges, a series of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored (no longer than 48 hours) as described in Section 9.10. For analysis the injection valve is placed in the load mode and the cryogenic loop is immersed in liquid nitrogen (or liquid argon if desired). The CMS cartridge is installed in the helium purge line (set at 50 mL/minute) so that the helium flow through the cartridge is opposite to the direction of sample flow and the purge gas is directed through the cryogenic loop and vented to the atmosphere. The CMS cartridge is heated to 370-400°C and maintained at this temperature for 10 minutes (using the temperature control process described in Section 9.8). During the desorption period, the GC column oven is cooled to -70°C and the MS and data system are setup for acquisition, but the ionizer filament is turned off.

11.3.7 At the end of the 10 minute desorption period, the analytical process described in Sections 11.3.4 and 11.3.5 is conducted. During the GC/MS analysis heating of the CMS cartridge is discontinued. Helium flow is maintained through the CMS cartridge and cryogenic loop until the cartridge has cooled to room temperature. At that time, the cryogenic loop is allowed to cool to room temperature and the system is ready for further cartridge analysis. Helium flow is maintained through the cryogenic loop at all times, except during the installation or removal of a CMS cartridge, to minimize contamination of the loop.

11.3.8 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved, the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.4 Sample Analysis

11.4.1 The sample analysis is identical to that described in Sections 11.3.6 and 11.3.7 for the analysis of standard CMS cartridges.

11.4.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reversed-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion). In general, quantities of components greater than 1,000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of three such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. In all cases one given standard concentration, near the midpoint of the analytical range of interest, should be injected at least once each day to determine day-to-day precision of response factors.

12.1.3 Since substantial nonlinearity may be present in the calibration curve, a nonlinear least squares fit (e.g. quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component injected nanograms
A, B, and C are coefficients in the equation.

12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX^2$$

where Y_A is the area of the analyte characteristic ion for the sample cartridge.
X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.
A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially linear over the concentration range of interest, a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_s}$$

where

C_A is the calculated concentration of analyte in ng/L.

Vs and X_A are as previously defined in Section 10.2.11 and 12.2.1, respectively.

13. Standard Preparation

13.1 Standards for Direct Injection

13.1.1 Standards for direct injection can be prepared in compressed gas cylinders or in dilution vessels. The dilution flask protocol has been described in detail in another method and is not repeated here (6). For the CMS method where only volatile compounds (boiling point <120°C) are of concern, the preparation of dilute standards in 15 liter aluminum compressed gas cylinders has been found to be most convenient. These standards are generally stable over at least a 3-4 month period and in some cases can be purchased from commercial suppliers on a custom prepared basis.

13.1.2 Preparation of compressed gas cylinders requires working with high pressure tubing and fittings, thus requiring a user prepared SOP which ensures that adequate safety precautions are taken. Basically, the preparation process involves injecting a predetermined amount of neat liquid or gas into an empty high pressure cylinder of known volume, using gas flow into the cylinder to complete the transfer.

The cylinder is then pressurized to a given value (500-1000 psi). The final cylinder pressure must be determined using a high precision gauge after the cylinder has thermally equilibrated for a 1-2 hour period after filling.

13.1.2 The concentration of components in the cylinder standard should be determined by comparison with National Bureau of Standards reference standards (e.g. SRM 1805-benzene in nitrogen) when available.

13.1.3 The theoretical concentration (at 25°C and 760 mm pressure) for preparation of cylinder standards can be calculated using the following equation:

$$C_T = \frac{V_I \times d}{V_c} \times \frac{14.7}{P_c + 14.7} \times 24.4 \times 1000$$

where C_T is the component concentration, in ng/mL at 25°C and 760 mm Hg pressure.

V_I is the volume of neat liquid component injected, in µL.

V_c is the internal volume of the cylinder, in L.

d is the density of the neat liquid component, in g/mL.

P_c is the final pressure of the cylinder standards, in pounds per square inch gauge (psig).

13.2 Preparation of Spiked Traps by Vapor Phase Injection

This process involves preparation of a dilution flask or compressed gas cylinder containing the desired concentrations of the compound(s) of interest and injecting the desired volume of vapor into a flowing gas stream which is directed onto a clean CMS cartridge. The procedure is described in detail in another method within the Compendium (6) and will not be repeated here.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion Tubes

13.3.1 A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609 (4). Note that a method of accurately maintaining temperature within ± 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean CMS cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed, they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3 The spiked traps are then stored or immediately analyzed as in Sections 11.3.6 and 11.3.7.

14. Performance Criteria and Quality Assurance

This section summarizes the quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g. parallel sampling).

14.1 Standard Operating Procedures (SOPs)

14.1.1 Each user should generate SOPs describing the following activities as accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, 2) preparation, handling and storage of CMS cartridges, 3) assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

14.2 CMS Cartridge Preparation

14.2.1 Each batch of CMS cartridges, prepared as described in Section 9, should be checked for contamination by analyzing one cartridge, immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may chose to use GC/FID due to logistical and cost considerations.

14.2.2 Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one-fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria, the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, having been placed in the sampler but without sampling air, to serve as a field blank. The average amount of material found on the field blank cartridges may be subtracted from the amount found on the actual samples. However, if the blank level is greater than

25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) should be collected, preferably at different flow rates as described in Section 10.1.4. If agreement between parallel samples is not generally within ±25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced sampling rate and longer sampling interval, if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest might be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass standardization have been discussed in Section 11.2 and Table 2. Additional criteria can be used by the laboratory, if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2 Chromatographic efficiency should be evaluated daily by the injection of calibration standards. A reference compound(s) should be chosen from the calibration standard and plotted on an expanded time scale so that its width at 10% of the peak height can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 6) should be between 0.8 and 2.0. The user should also evaluate chromatographic performance for any polar or reactive compounds of interest, using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings or tubing and/or if replacement of the GC column is required. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7).

14.4.3 The detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required). The lowest level standard should yield a signal to noise ratio (from the total ion current response) of approximately 5.

14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation for replicate cartridges should be 25% or less.

14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present is ambient air (e.g. perfluorotoluene). Spiking is readily accomplished using the procedure outlined in Section 13.2, using a compressed gas standard. The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ± 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

14.5 Method Precision and Recovery

14.5.1 Recovery and precision data for selected volatile organic compounds are presented in Table 1. These data were obtained using ambient air, spiked with known amounts of the compounds in a dynamic mixing system (2).

14.5.2 The data in Table 1 indicate that in general recoveries better than 75% and precision (relative standard deviations) of 15-20% can be obtained. However, selected compounds (e.g. carbon tetrachloride and benzene) will have poorer precision and/or recovery. The user must check recovery and precision for any compounds for which quantitative data are needed.

References

1. Kebbekus, B. B. and J. W. Bozzelli. Collection and Analysis of Selected Volatile Organic Compounds in Ambient Air. Proceedings of Air Pollution Control Association, Paper No. 82-65.2, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1982.

2. Riggin R. M. and L. E. Slivon. Determination of Volatile Organic Compounds in Ambient Air Using Carbon Molecular Sieve Adsorbants, Special Report on Contract 68-02-3745 (WA-7), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September, 1983.

3. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

4. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis: Occupational Health and Safety", American Society for Testing and Materials, 1983.

5. Walling, J. F., Berkley, R. E., Swanson, D. H., and Toth, F. J. "Sampling Air for Gaseous Organic Chemical-Applications to Tenax", EPA-600/7-54-82-059, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

6. This Methods Compendium - Tenax Method (TO 1).

7. Grob, K., Jr., Grob, G., and Grob, K., "Comprehensive Standardized Quality Test for Glass Capillary Columns", J. Chromatog., <u>156</u> 1-20, 1978.

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CMS ADSORPTION METHOD HAS BEEN EVALUATED

Compound	Retention Time, Minutes(a)	Characteristic Mass Fragment Used For Quantification	Method Performance Data(b) Concentration, ng/L	Percent Recovery	Standard Deviation
Vinyl Chloride	6.3	62	17	74	19
Acrylonitrile	10.8	53	20	85	18
Vinylidene Chloride	10.9	96	36	94	19
Methylene Chloride	11.3	84	28	93	16
Allyl Chloride	11.4	76	32	72	19
Chloroform	13.8	83	89	91	12
1,2-Dichloroethane	14.5	62	37	85	11
1,1,1-Trichloroethane	14.7	97	100	75	9.1
Benzene	15.4	78	15	140	37
Carbon Tetrachloride	15.5	117	86	55	2.9
Toluene	18.0	91	4.1	98	5.4

a) GC conditions as follows:

Column - Hewlett Packard, crosslinked methyl silicone, 0.32 mm ID x 50 mm long, thick film, fused silica.

Temperature Program - 70°C for 2 minutes then increased at 8°C/minute to 120°C.

b) From Reference 2. For spiked ambient air.

TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

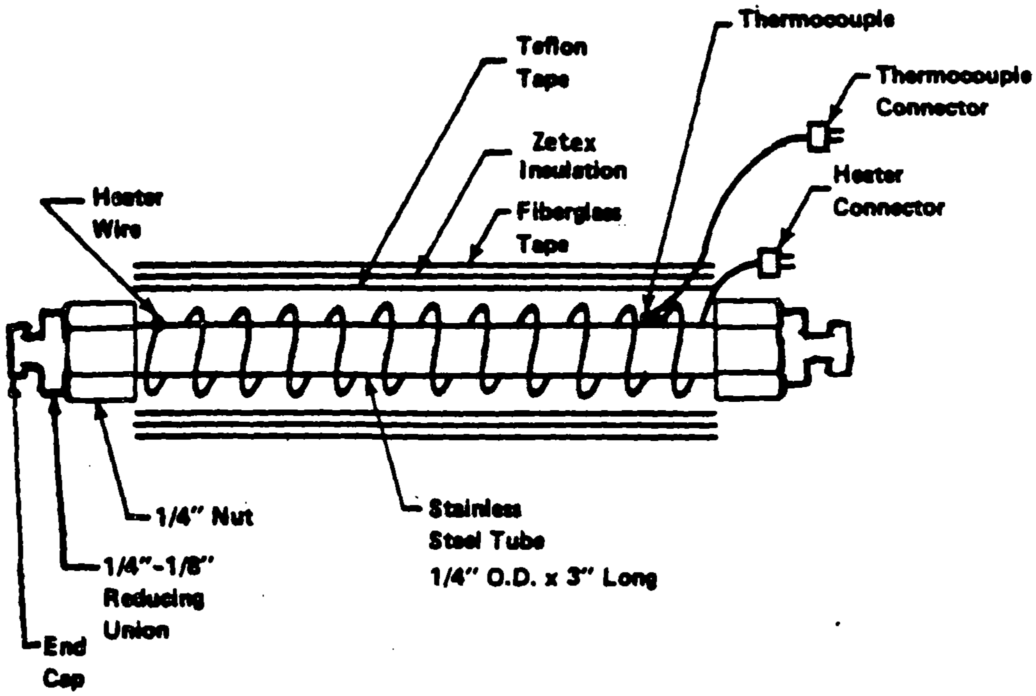
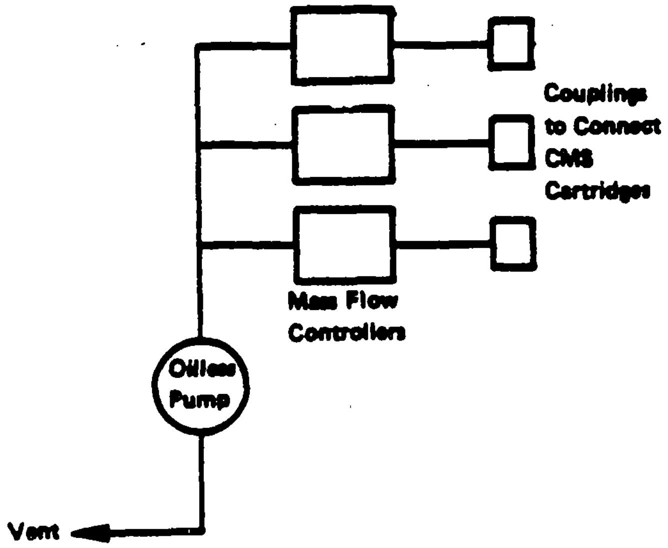
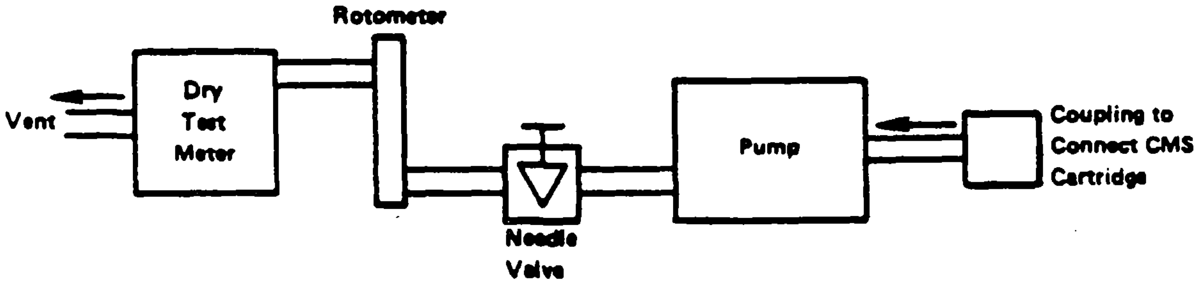


FIGURE 1. DIAGRAM SHOWING CARBON MOLECULAR SIEVE TRAP (CMS) CONSTRUCTION

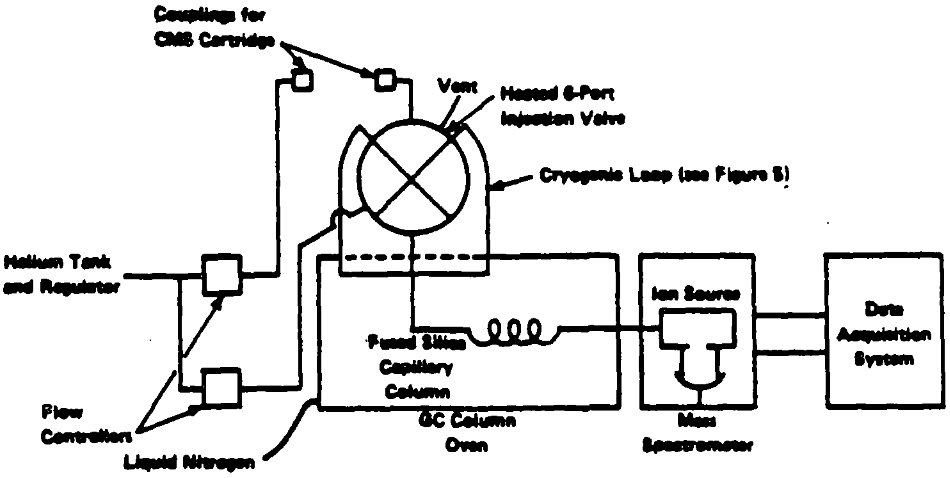


(a) Mass Flow Control

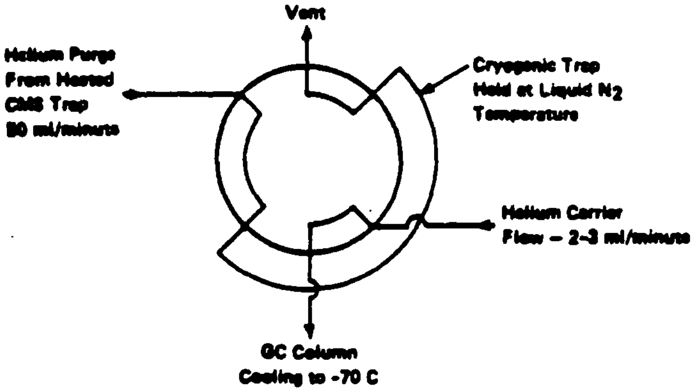


(b) Needle Valve Control

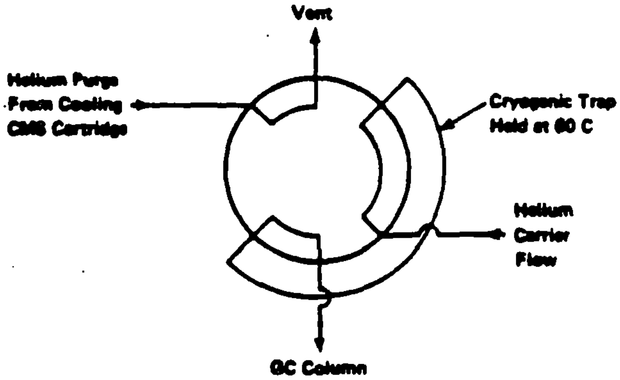
FIGURE 2. TYPICAL SAMPLING SYSTEM CONFIGURATIONS



(a) Overall System



(b) Valve – Load Mode



(c) Valve – Inject Mode

FIGURE 3. GC/MS ANALYSIS SYSTEM FOR CMS CARTRIDGES

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

PROJECT: ______________________

SITE: ______________________

LOCATION: ______________________

INSTRUMENT MODEL NO: ______________

PUMP SERIAL NO: ______________

DATE(S) SAMPLED: ______________________

TIME PERIOD SAMPLED: ______________

OPERATOR: ______________________

CALIBRATED BY: ______________________

SAMPLING DATA

Sample Number: ______________________

Start Time: __________ Stop Time: __________

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q ml/Min	Ambient Temperature °C	Barometric Pressure, mmHg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = ______ Liters

$$\frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_\_ \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

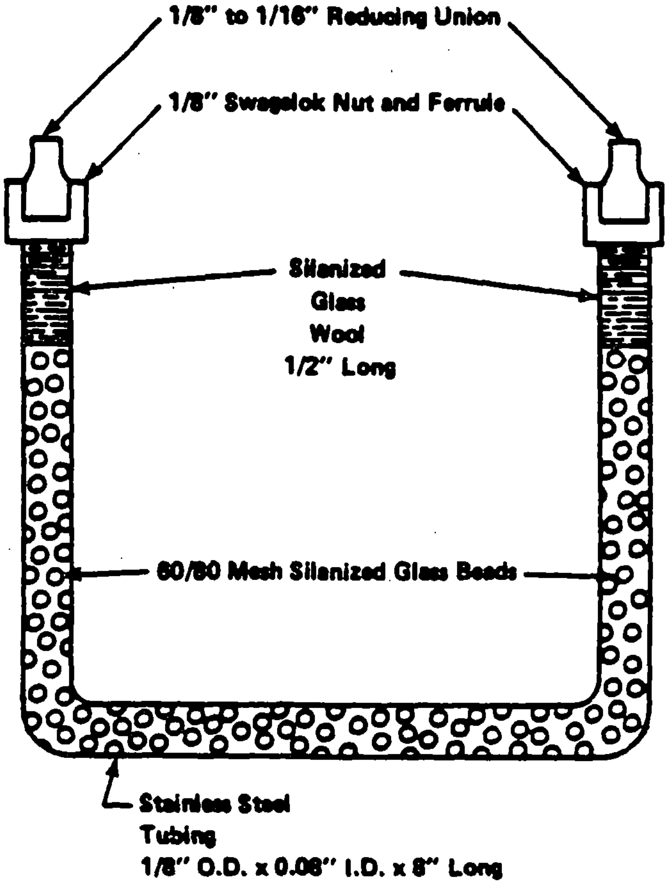
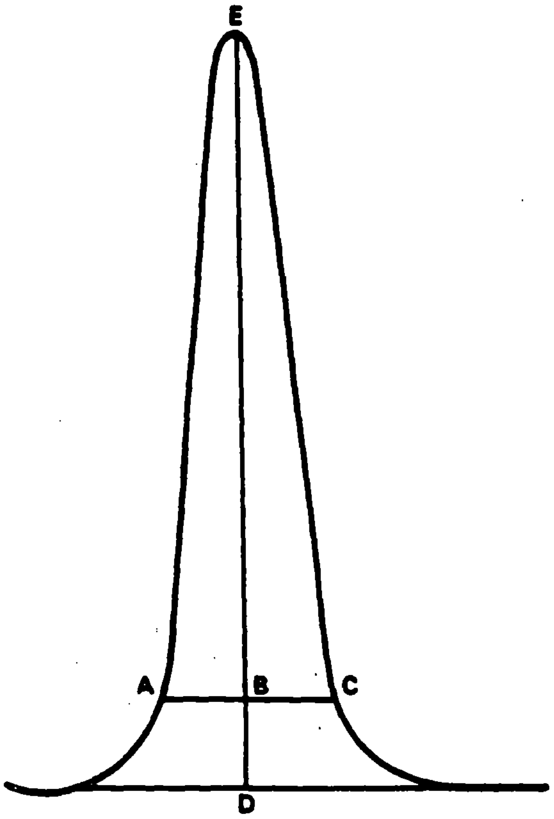


FIGURE 5. CRYOGENIC TRAP DESIGN

SRC

glass $27.50
steel $44.00

steel $44.00



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11} = 1.1$

FIGURE 6. PEAK ASYMMETRY CALCULATION