2.2 ASBESTOS MEASUREMENTS

2.2.1 Current Methodology

Six asbestos minerals occur in nature that are used in commerce. One, chrysotile, is from the serpentine group and comprises over 95% of the asbestos mined in California (Ref. 16). Antigorite and lizardite are non-asbestiform serpentines that are chemically identical with chrysotile. Five fibrous amphiboles are found of which crocidilite and amosite are the most common. Anthophyllite, tremolite and actinolite are more rare and exhibit both asbestiform and nonasbestiform habits. Other nonasbestiform amphiboles include riebeckite, cummingtonite and grunerite.

The asbestos minerals are all silicates, but otherwise chemically and morphologically different from one another. They are, however, easily confused with one another and with their non-asbestiform counterparts, which are acicular or needlelike in structure.

The techniques generally employed for counting fibers of asbestos on filters involve microscopy. Conversion from fibril counts to weight terms is accomplished by applying fiber densities to the distribution of particle sizes observed. An obvious weakness in the microscope is that the size distribution for an entire sample must be assumed from the counts for a relatively small fraction of the total fields.

Phase-contrast optical microscopy with or without the use of dispersion staining is popular in the industrial hygiene field. The NIOSH recommended microscopic procedure (P & CAM No. 239) involves this technique. Optical microscopy has been widely criticized because the predominant fraction of environmental asbestos fibrils are smaller (<0.5 um) than the resolving power of the optical microscope (Refs. 17-22). Thus, its use results in counts for only the upper end of the respirable range (<15 µm) of fibrils. Because of this,optical microscopy is generally discounted as furnishing results that are badly biased to the low side (Refs. 17-22).

Other techniques that have been applied include infrared (IR) absorption, X-ray diffraction (XRD), and differential thermal analysis (DTA). These are all relatively insensitive methods (Ref. 23).

Of the electron microscopic techniques generally applied, the transmission electron microscope (TEM), which is capable of furnishing selected area electron diffraction (SAED) patterns, dominates. The scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopic (EDXS) system is also employed. TEM-SAED system is preferred, since, for one thing, it furnishes crystallographic identifications of the microfield fibrils. The SEM-EDXS provides elemental chemical analysis of the irradiated target, which can prove equivocal when verifying mineral structures.

2.2.2 Problems with the Methodology

As the recognized favored technique for asbestos measurement, the TEM-SAED approach had been and is still being used without benefit of technique standardization. The EPA recognized this and sought in 1977 to determine how closely practitioners at leading laboratories would count the same prepared samples. The results, shown in Table 2-1, verge on the ludicrous (Ref. 24). The National Emissions Standards for Hazardous Air Pollutants (NESHAPS) thus states:

> "It is not practicable, at this time, to establish allowable numerical concentrations or mass emission limits for asbestos. Satisfactory means of measuring asbestos emissions are still unavailable."

The EPA consequently awarded a contract to Illinois Institute of Technology Research Institute (IITRI) to conduct a study of the TEM-SAED method and develop an optimized version that could then be applied as a standardized procedure. IITRI systematically evaluated the many facets of the method and, in addition to reporting its findings (Ref. 25), produced a manual that has subsequently undergone one revision (Ref. 26).

The method uses a polycarbonate membrane filter to collect ambient air fibers. The filter is then coated with a thin (conductive) layer of carbon in the vacuum deposition chamber. The process is then transferred to a 200 mesh EM microscope grid, the filter being dissolved off with chloroform in a modified Jaffe washer. The grids are examined in the TEM at a screen magnification of 16,000X. Each filter is characterized from its morphology

TABLE 2-1

RESULTS OF TEM-SAED CHRYSOTILE COUNTING IN EPA-SPONSORED ROUND ROBIN

Mass (Volume/density basis)
ng/m^3

Sample #	McCrone	EPA Duluth	Bureau of Mines	Battelle
1	BDL*	2.24	65	0.31
2	BDL	BDL	30	4.3
3	BDL	14.2	--†	7.6
11	BDL	1.31	43	56
12	137	87.5	83	207
13	2.1	12.0	28	162
21	131	31.1	304	183
22	0.79	2.77	128	633
23	0.76	4.99	88	614

* Below Detectable Level

† No value reported

and SAED pattern. The counts are segregated into chrysotile, amphibole and non-asbestos categories. Counts are enumerated by field-of-view method. Where mass concentration is required, the length and width of each fiber is recorded and entered into a computer program. A subroutine is also provided for samples containing high levels of organic contaminant. This consists of ashing the sample in a low temperature (microwave) ashing chamber. The residue is dispersed in water by ultrasonication and is recollected on a new filter, which is then processed in the same manner as regular samples.

Prior to revision, the IITRI method was tested for ruggedness by six laboratories. Two samples were measured, one artificially prepared and the other collected outside an asbestos processing plant. The coefficient of variation for the round robin was 21% for both samples in the fiber counting. In mass concentrations, the C_v was 22% for the prepared sample and 44% for the field sample when the ashing subprocedure was used. Omitting the ashing step caused the C_v to deteriorate to 54% for the field sample.

On the same round robin an attempt was made to determine the accuracy of the results obtained. Chrysotile, having the chemical formula of $Mg_3(Si_2O_5)(OH)_4$ is 26.3% magnesium. Thus, on measuring the concentration of that alkaline earth metal by x-ray fluorescence (XRF) on the filters, a mass could be computed. In the case of the prepared samples, the mean mass value for the six labs agreed within 10% of the XRF-derived value. In the field sample the XRF value was 4.2 times higher than the mean.

The logic of establishing a true value for asbestos using chemical (XRF) analysis is apparent in the case of the prepared sample, which contained only purified chrysotile on a magnesium-free substrate. The field sample consisted of particulates from a factory where asbestos and Portland Cement are blended. The latter, of course, contains considerable magnesium which would certainly interfere in the scheme. Thus, the results of this accuracy testing were actually quite encouraging even if the approach was obviously inapplicable to the field sample.

The method has not been reexercised since revisions were made to it and the IITRI authors, when contacted by telephone by KVB project workers, acknowledged that they do not expect better results with the new version since the changes introduced were not very substantive. The EPA, however, is currently in the process of letting a contract to thoroughly test the ruggedness of the provisionary method.

2.2.3 Recommended Approach

Although the IITRI method (Ref. 26) has not been adequately exercised, preliminary ruggedness trials showed considerably better results than those previously obtained. According to Dr. Jack Wagman, Director of the EPA's Emissions Measurement and Characterization Division at Research Triangle Park, new methods are being evaluated. At SRI, attempts are underway to extend the sensitivity of XRD for asbestos analysis using fiber optical modifications in the system. This work is far from term and may not eventuate in success.

It is therefore apparent that the TEM-SAED provisional EPA method developed by IITRI should be employed until a superior technique has been developed and proved. It will be highly important, however, that modifications or compromises to the method be avoided. Because of the state of affairs that existed before the EPA attempted standardization, the TEM art was practiced in a rather subjective and independent manner. It will be important, therefore, to avoid practitioners who promote their own "superior" techniques over standardized ones.

2.2.4 Laboratory Qualifications

The qualified laboratory must offer experience in practicing the EPA provisional asbestos method. This implies availability of a TEM capable of 100 kv of accelerating voltage, 1 nm resolution, and a magnification range of 300 to 100,000X. The instrument should be capable of SAED analysis on areas of 300 nm dia. The fluorescent screen should have either a millimeter scale, concentric circles of 1, 2, 3, and 4 cm radii, or other suitable scalings.

Vacuum evaporation equipment, of the nonsputtering type, equipped with fully rotating turntable is also required. A low-temperature plasma asher, equipped with an oxygen inlet system and offering a sample chamber at least 10 cm dia., is further required. Other minor equipment items are specified in the provisional manual.

An in-place and properly operated quality assurance program must be demonstrated by any laboratory otherwise qualified to perform TEM-SAED analysis. The scope of such QA activities is discussed in Section 2-8.

2.3 BENZENE ANALYSIS

2.3.1 Nature of the Methodology

The technique in essentially general use for determining benzene is gas chromatography (GC). This procedure also furnishes quantitations of other constituents present in the sample provided that such analytes are volatile under the GC conditions used and produce adequate signals in the detectors employed. For more sensitive work, the flame ionization detector (FID) is preferred. The thermal conductivity (TC) detector can be employed with samples containing higher levels of benzene. Certain other detectors, such as the photoionization and Martin differential density detectors, can also be used.

Benzene is not usually sought as an individual analyte, but rather as merely a member of various mixtures, often of routine interest to different industries. As a result of this, and the art-like approach to GC separations, a host of successful operating conditions has evolved. This includes the use of different column characteristics, such as packings (polymer bead types now seem more popular than supported liquids), geometries (length and I.D.), materials (copper is quite satisfactory, although stainless steel is usually preferred), and type (packed or capillary, the latter being preferred for complex mixtures). Different temperature (isothermal or programmed) conditions can be used as determined by the column characteristics and the volatile range and polarity of the other constituents in the sample.

Introduction of the sample into the GC system can be done in several ways. In the case of environmental samples, this may include gas samples and sorbent tubes. The former, contained in bags (often tedlar) or glass sampling bulbs, can be aliquoted with a manometric gas loop (incorporated in the GC system) or a gas syringe. If a gas loop is used, simple aliquoting may prove inadequately sensitive (gas loops usually are less than 5 ml in volume). In this case a cryotrap can be employed wherein all or a large portion of the gas sample is passed through the loop, the benzene and other condensables collecting in the trap. This concentrate is then expanded by heating and introduced onto the column in the usual manner.

Sorbent tubes may be thermally desorbable (e.g., Tenax) or require extraction with a solvent (e.g., charcoal). In the former case, all of the catch goes into the instrument, providing excellent sensitivity, but with no opportunity for replication except with other tubes loaded in parallel from the same source. Where a tube is extracted, aliquoting is again necessary. Using carbon disulfide as the solvent (because of its negligible FID response), one ml is used to remove the adsorbates on a standard personal sampler tube (e.g., NIOSH P & CAM method No. 127). Of this only about 5 µl are injected into the GC septum, such that only 0.5% of the benzene in the volume of air drawn through the sampling tube is worked in the analysis. Replication is facile, however, provided solvent evaporation is prevented or compensated for.

In any of the above sampling modes, the GC analysis must be accompanied by appropriate instrument calibration procedures. This can be done by solution techniques (syringe injection) or by the use of calibration gas containing known amounts of benzene. Furthermore, however, recovery factors must be applied when using sorbent tubes. In the case of thermal desorption, not all of the analyte is removed. In extraction (batch) techniques, a partitioning effect operates which predicts that some of the analyte must remain on the sorbent as determined by its adsorption isotherm. Thus correction factors must be applied that have been experimentally determined for each lot of sorbent.

In working with sorbent tubes, it is also very important to run blanks. Activated charcoal used as sampling sorbent is notorious with respect to benzene. Despite all attempts to purify the material, benzene can almost always be detected in a blank run. Polymer sorbents are less noted for this behavior, but being chemical "sponges" are very prone to contamination.

Given a suitable GC instrument and operating conditions, and applying the necessary correction factors, a coefficient of variation of 5.9% is reported by NIOSH in its benzene charcoal tube method, P & CAM No. S311. Fairly high levels of benzene (26-104 mg/tube) were used, however. The accuracy noted was +0.8%; that is, a slight positive bias with respect to the truth was observed.

Benzene is also an analyte that is tested on NIOSH's Proficiency Analytical Testing (PAT) Program. On two recent rounds (54 and 55) of this round robin 175 labs participated. The coefficient of variation (about the grand mean or concensus) ranged from 11.6% up to 23.3% as concentration decreased from about 63 µg to 7.5 µg per sorbent tube. Oddly enough, the detection limit of benzene specified in NIOSH P & CAM No. 127 is 10 µg/sample, which is above the bottom of the PAT range just cited. In discussing detection limit, incidentally, aliquot ratio should be borne in mind. Since only 0.5% of the analyte is actually committed to the FID, the detection limit of the latter is 50 ng (or less), not 10 µg.

2.3.2 Analytical Problems

As is true of any GC analysis, analyte identification depends on the retention time or volume of the eluted material. Mistaken assignments are commonplace, particularly when the chromatograms show multiple, including fused, peaks in the zone where the material of interest is expected. If this problem cannot be corrected by employing superior GC conditions, as through the substitution of a column furnishing greater plate efficiency, then other corrective procedures become necessary. A simplistic remedy is to spike the sample (lightly) with the analyte and thus confirm its now accepted position in the pattern. A superior technique is to run the sample on two different columns that will tend to rearrange constituent elution times due to designed substrate polarity differences. The preferred approach is to use a GC tandemized with a mass spectrometer (MS) equipped with a computerized data system (DS), including cracking pattern library. The GC/MS-DS will usually provide an unequivocal assignment for the analyte and furnish a semiquantitative analysis. By using the same GC conditions on the GC/MS-DS as were employed in the regular GC analyses, peak identification of the FID chromatogram is then possible. Quantitation should then proceed using the GC-FID data.

2.3.3 Recommended Approach

Any GC technique that has a demonstrated capability of adequately resolving benzene from, say, gasoline vapor and furnishing adequate detectivity, precision and accuracy may be employed.

2.3.4 Laboratory Qualifications

Assuming that an acceptable QA program is effectively in place (see Sec. 2.8), any laboratory offering professional GC analytical services and requisite instrumentation should qualify for benzene analysis. Because sample concentration may range over a considerable span, it will be desirable that both FID and TC-detector-equipped GC systems be available.

Data reduction by manual techniques will not be acceptable. An electronic integrator designed for GC service and incorporating the necessary logic for performing the basic geometric options used in fused-peak integrations will be required. It will also be highly desirable that the laboratory be able to verify peak assignments using a GC/MS-DS operated by a competent analyst.

2.4 CADMIUM ANALYSIS

2.4.1 Nature of the Methodology

Until the appearance of AAS, colorimetry was the most widely utilized technique for determining cadmium (Ref. 27). The most popular technique involves the extraction of cadmium ion from a buffered aqueous system into dithizone/chloroform. The cadmium dithizonate is read at 620 nm.

Spectroscopic techniques include AAS (flame and graphite furnace), emission (arc, spark, flame and plasma) and spark source mass spectrometry (SSMS). The last is semiquantitative, except when isolation dilution is employed in which case 5% accuracy can be expected (Ref. 28). The SSMS method is quite sensitive, virtually free of matrix effects and can determine many elements simultaneously. It is also quite expensive.

Of the emission spectrographic techniques, ICP*analysis is considerably more sensitive and accurate than the conventional arc or spark source methods (Ref. 29). Unless, however, multielement analysis is desired, equivalent results can be obtained by AAS at less cost.

Using flame emission techniques, atomic emission, atomic absorption, and atomic fluorescence modes can be used. Detection limits are reported, respectively, at 50, 10 and 0.2 ng/ml of prepared solution (Ref. 28). These limits can be extended by preconcentration of the cadmium or by using a longer burner (for AAS mode). Graphite furnace AAS, however, affords superior detectivity without the need of such "extenders."

Of the electrochemical techniques, differential pulse polarography and anodic stripping voltammetry are preferred for cadmium analysis. The former is capable of detecting as little as 4 ng of cadmium per ml of prepared solution (Ref. 30). With anodic stripping voltammetry, slightly better sensitivity is achieved. Accuracies of ±10% are available from these electrochemical procedures.

Neutron activation analysis (NAA) will quantitate cadmium although sensitivity is not as great as for other of the elements. Being an expensive technique, application of NAA is used only if nondestructive and multielement analysis is sought.

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*Inductively coupled plasma (argon) emission spectroscopy

X-ray fluorescence analysis is also suboptimum for cadmium. Cadmium is poorly excited by conventional x-ray systems (Ref. 31). It is, however, non-destructive and has multielement capability.

2.4.2 Recommended Approach

The NIOSH recommends either anodic stripping voltammetry or AAS (P&CAM Nos. 173, S312 and S313). While flame AAS is considerably less sensitive than anodic stripping, graphite furnace AAS has about an equivalent detection limit with respect to the latter. NIOSH precision data included with their method descriptions show precisions of 5 and 6% for either method. This is consistent with results obtained on the PAT program, which includes cadmium as an analyte.

Using flame AAS, the EPA reports (Ref. 32) round robin (51 to 74 labs) accuracies within less than 20% (less than 5.7% in 80% of the data) for sample concentrations above 2 ng/ml. In the same range, graphite furnace AAS analyses would be expected to be better since the range is well above detection limit which was not the case in the flame round robin.

Because other methods suffer from high cost or sensitivity limitations, and because the methodology discussed here appears to be relatively problem-free, both the voltammetric or AAS approach are recommended. In the latter case, however, where final working solutions drop in cadmium concentration below 50 ng/ml, the graphite furnace technique should be used.

Being a relatively volatile metal, dry ashing of cadmium should be avoided (Ref. 32). A nitric acid digestion under reflux is usually adequate, although low temperature plasma (microwave) ashing is also acceptable.

2.4.3 Laboratory Qualifications

For AAS analysis see Section 2.1.4. Cadmium is measured at 228.8 nm but is strongly self absorbing at this line. The hollow cathode lamp should, therefore, be operated at a relatively low current.

For voltammetric analysis a single or multiple cell anodic stripping voltammeter equipped with composite mercury-graphite electrode (s) shall be used. The Environmental Sciences Associates Model SA 2011 or equivalent is acceptable. Analyses must be conducted by or under the supervision of a trained electrochemist.

2.5 HALOCARBON ANALYSIS

2.5.1 Nature of the Methodology

As with benzene, the analysis of the five halocarbons studied on this program is almost exclusively accomplished using GC. Thus, the discussion in Section 2.3 on benzene is also applicable here. For carbon tetrachloride analysis, which provides the poorest FID response of the five halocarbons, the NIOSH P&CAM No. S314 for that analyte is substantively the same method as for benzene analysis. In the latter case, Poropak Q is specified as the column packing while the CT method specifies about the same packing recommended for general solvent analyses, which is 10% FFAP on 100/120 mesh Supelcoport (see P&CAM No. 127). This is also true of the P&CAM methods for chloroform and EDB. In the case of perc and EDC, the method developer chose to use 10% OV-101 as the stationary phase. In each case, however, the FID is specified as the detector.

2.5.2 Analytical Problems

The analytical problems discussed under Benzene Analysis (Sec. 2.3) apply to halocarbons or to any GC determination. In terms of source sampling, however, halocarbon analysis should not involve complex mixtures as would occur in sampling for benzene at a refinery.

A problem that may be encountered in halocarbon analysis is FID sensitivity. All five of the halocarbons of interest exhibit sensitivities that are considerably lower than those of hydrocarbon analytes. Compared to benzene, for example, over twenty times as much CT is required to furnish the same FID response.

If the relatively lower sensitivity of the halocarbons proves problematic, then the electron capture detector (ECD) or conductimetric (Hall) detector should be employed. If the ECD is used, however, it must be of the constant current (variable pulse frequency) type. The old-design ECD's, which operate in the fixed pulse modality, have such limited linear dynamic ranges as to make them unreliable for other than qualitative work.

The ECD and Hall detectors furnish sensitivities at least three orders of magnitude better than the FID for the compounds of interest. They also offer the advantage of greater selectivity. The Hall detector responds only to halocarbons and a few other classes of compounds that are rarely encountered. The ECD responds to electronegative chemicals, which precludes responses to most nonaromatic hydrocarbons.

2.5.3 Recommended Approach

Any GC technique that has a demonstrated capability of adequately resolving the analyte of interest and furnishing the required detectivity, precision, and accuracy may be used.

2.5.4 Laboratory Qualifications

See Benzene Analysis (Sec. 2.3.4). Additionally, if an ECD is employed for the analysis, it shall be equipped with electronics furnishing constant current (variable pulse frequency) such as offered by Analog Technology, Inc. or equivalent. A linear dynamic range of 10^5 should be available.

2.6 NITROSAMINE ANALYSIS

2.6.1 Nature of the Methodology

A variety of techniques have been employed in the analysis of nitrosamines in various media. These include colorimetry, UV absorption, polarography, thin layer chromatography, fluorimetry, gas chromatography and mass spectrometry (Ref. 33). Many of the earlier methods were of doubtful value because of susceptibilities to interferences. As interest in nitrosamines has grown in recent years, more reliable methods have appeared. The techniques that have been adopted by government agencies are all based on GC. The principal variable in this methodology is the detector.

Dure employed the N-selective thermionic FID (Giuffrida) system for volatile nitrosamine analysis (Ref. 34). The technique, while quite sensitive, did not catch on, possibly because of the notoriety of the thermionic detector with respect to drift. Fine and his coworkers developed the thermal energy analyzer (TEA) detector (Ref. 35). The system consists of a chemiluminescence analyzer using ozone as the reagent gas. N-nitroso compounds are catalytically pyrolyzed to form amine and nitrosyl radical . The latter is oxidized to metastable NO_2, which emits in the IR region on returning to ground state. The TEA detector has been adapted for use with both GC (Ref. 36) and high pressure liquid chromatography (Ref. 37). The detectable limit for the GC-TEA method is estimated at about 0.05 $\mu g/m^3$ based on using a 2% aliquot of a concentrated scrubber solution containing the nitrosamines from 2 cu ft. The combination of the GC separation effect and the rather unique nitrosyl radical forming process make the TEA analysis essentially interference free.

A second method used has been evaluated by Research Triangle Institute (RTI). In this procedure, a sorbent tube packed with Tenax is exposed to a sample air stream, then is thermally desorbed (in reverse direction of flow) into the GC/MS-DS (Ref. 38). Since no aliquoting is involved, all of the available adsorbed analyte is committed to the analysis. The NIOSH has adopted the RTI procedure as a proposed method (P&CAM No. 252). They have found the detection limit to be about 5 ng/m^3, based on sampling 2 cu ft of air. This is ten times more sensitive than the TEA method which, however, commits only 1/50th of the sample. At 50x detection limit, the NIOSH reports a standard deviation of ±10% and a like error for accuracy with the RTI method.

The TEA and RTI methods have been compared in the field (Ref. 39) at three different sites within Baltimore. Although the samples were not taken simultaneously, the results agreed reasonably well.

2.6.2 Analytical Drawbacks

Both of the favored methods (TEA and GC/MS-DS) are less susceptible to the problems associated with GC analysis (see Sec. 2.3.2) because of the selectivity of the detectors used. In the case of the GC/MS-DS analysis, nitrosamine identification may be confused by the coelution of any compounds producing positive ions of the same mass to charge (m/e) ratios as those principal ones comprising the diagnostic cracking pattern of the nitrosamine. This problem is largely overcome by the use of high resolution GC conditions, as specified in the RTI method.

A principal drawback of these two procedures is equipment cost. The GC/MS-DS, is considerably more expensive than the TEA system, but the latter, unless disassembled or modified, offers little other functionality than for nitrosamine analysis. Thus the availability of both instruments is somewhat restricted. The attractiveness of the GC/MS-DS for general lab use is bringing it into more and more labs despite its high cost.

2.6.3 Recommended Approach

Either the TEA method as described in Reference 36 or the RTI method as described in Reference 38 or the NIOSH Manual of Analytical Methods (P&CAM No. 252) are recommended.

2.6.4 Laboratory Qualifications

Assuming that an acceptable QA program is effectively in place (see Sec. 2.8), any laboratory having the requisite instrumentation to perform the recommended procedures should be qualified. In the case of the TEA, the only equipment acceptable is the TEA Model 502 offered by the Thermo Electron Corporation.

For GC/MS-DS analysis, a low resolution MS (to m/e 800) coupled with a high resolution GC system and data system is basic. Varian, Finnigan, DuPont, and others offer systems that will furnish the performance specifications described in Reference 28. Software used must of course furnish m/e files for the materials of interest and a capability of furnishing pattern fit assessments for all scans produced. The quadrapole or magnetic analyzer must be capable of producing a scan at least once a second. The software will also include routines for performing peak integrations for single ion as well as total ion current traces.

The computer system should also be equipped with m/e storage capacity that will permit the saving of all data from GC/MS runs.

2.7 POLYCYCLIC ORGANIC MATTER (POM) ANALYSIS

2.7.1 Nature of the Methodology

Expectedly, a survey of the state of the art reveals the dominance of chromatographic procedures in the analysis of POM (Ref. 40). This applied art ranges from thin layer chromatography (TLC), through liquid and gas chromatography, to GC/MS-DS technique in both the electron impact (EI) and chemical ionization (CI) modes of operation.

In industrial hygiene matters, the NIOSH has published four methods for POM analysis; three, P&CAM Nos. 183, 184 and 186, are operational, while the fourth has proposed status. P&CAM No. 183 utilizes a gas chromatograph equipped with 10:1 splitter. The minor stream serves an FID while the major stream terminates in a fraction collector. The fractions corresponding to POM signals are quantitated by UV spectrophotometry. In P&CAM No. 184 quantitation is the same as in P&CAM 183; the fractions, however, are furnished by an LC column with gradient (n-pentane/ether) elution. P&CAM No. 186 utilizes TLC and only benzo(a)pyrene (BaP) is quantitated. The spot is visualized by UV irradiation and the extract of the scrapings measured on the spectrophotofluorimeter. In P&CAM No. 206 high performance liquid chromatography (HPLC) is employed in conjunction with a UV detector capable of sensing 3 ng of BaP. Recovery data for some 29 polycyclic aromatic hydrocarbons are given; these range from 91% to 105%. In summary, then, all of the NIOSH procedures involve photometric quantitation.

In contrast, workers in the air pollution field have tended to use GC techniques with conventional detectors (FID) or, more recently, in the GC/MS-DS configuration. Because of the complexity of POM and the previous partitioning limitations of the columns used, earlier GC work was preceded by coarse LC fractionations (e.g., Ref. 41). With the discovery of superior stationary phases and the introduction of high plate efficiency (capillary) columns, the need for preliminary class separations has been eliminated. Lao et al, using Dexsil packed columns, were able to resolve, but not to baseline, problem compounds that in previous experience always coeluted (Ref. 42). These are benzo(a)anthracene (BaA)/chrysene and BaP/BeP.

Capillary columns provide considerably better separations than packed columns. At Battelle, coated capillary columns have furnished baseline separations of the two pairs discussed above, as well as phenanthrene from anthracene. Furthermore, partial separation is achieved for benzo(b)fluoranthene from its j and k isomers. The Battelle procedure is described in Appendix A.

Battelle is providing POM analyses to KVB in a current study to characterize POM in power plant effluents. This work is being funded by the Electric Power Research Institute (ERPI) on Contract No. RP 1075-1. In evaluating the reliability of the procedure used, Battelle reported (Ref. 43) an average recovery of 92% for the nine compounds of interest. The technique described in Appendix A is, however, capable of resolving POM into hundreds of components. Sensitivity of the GC/MS-DS is a few nanograms of POM injected. Aliquoting will of course decrease sensitivity when expressed in terms of the sample solution.

2.7.2 Analytical Problems

The category designated as POM is a highly complex system due to its definition. As stated in the Ref. 40 discussion, confusion exists as to the specific chemical classes that are incorporated. The EPA defines (Ref. 44) POM to include the true polycyclic aromatic hydrocarbons (PAH), plus aza and imino (the terms are synonymous), arene (generic term for monocyclic as well as fused ring aromatic hydrocarbons), related heterocyclic (nitrogen, oxygen, sulfur ring atoms) and alicyclic species, plus any of these molecules with side groups with or without functional activity.

Because of the wide range of vapor pressures and adsorptive properties of this defined POM, it is simply impossible to propose a chromatographic process that will adequately separate and elute all possible members. Thus P&CAM 206 points out that fluorene (2,3-benzindene) elutes in 2 minutes from the HPLC column used with 100% recovery. The alcohol, 9 hydroxyfluorene, elutes in 8.5 minutes but with only 14% yield; the phenol, 2-hydroxyfluorene, does not elute at all; nor do the ketone (9-fluorenone) or the 4-carboxylic acid. Similarly, capillary GC will elute POM hydrocarbons* of up to C_{30} ring

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* By strict definition, hydrocarbons contain only carbon and hydrogen.

structure (Ref. 45). This seems impressive enough except that this distillation range would drop drastically with the introduction of hetero atoms or functional groups into or onto the molecular structures involved. In ambient air, POM is known to form nitro compounds. This could also occur in stacks, the present context, and again frustrate analytical determination.

Because of this, the comprehensive analysis of POM really becomes a research project. This would involve chemical classification, group partitioning, liquid chromatography, and then GC/MS analysis of some fractions directly and others only after the constituents had been made more volatile through derivatizations. Thus, for practicable survey purposes, one must apply those available methods that furnish the most information with reasonable reliability.

2.7.3 Recommended Approach

The method described in Appendix A is recommended for use.

2.7.4 Laboratory Qualifications

See Nitrosamine Analysis Section 2.6.4. The discussion on TEA requirements does not apply here. For POM analysis, a system equipped with a capillary column must be used.

2.8 QUALITY ASSURANCE - LABORATORY

In performing the analytical methods discussed in this section, quality control practices must be applied at various stages of the laboratory operations. This will involve:

- Sample receipt and accountability system
- Application of appropriately documented and recommended methodology
- Utilization of nonchallengeable data handling, recording, and reporting procedures
- Implementation of a schedule of calibration and maintenance routines for all instrumentation and measuring devices
- Employment of chemical standards of primary or traceable reliability
- Evaluation and approval/recycle of work based on accepted variance analysis techniques
- Frequent testing of worker competence by injection of check samples and participation in available round robins
- Maintenance of staff capabilities through appropriate training and retraining activities

The realization of these objectives can only be accomplished through the exercise of a QA program. Such a program must be nurtured and not just tolerated by top laboratory management. The QA program should be headed up by a QA coordinator who, preferably, has no collateral assignments and certainly none posing conflict of interests. The QA coordinator should report to the highest placed individual in the laboratory management system.

The QA program shall be organized in manual form and provide the QC elements contained in the Quality Assurance Handbook for Air Pollution Measurement Systems (U.S. EPA-600/4-77-027a).

Evaluation of a QA program as being effectively in place should not depend on the results of other inspectors. Even government surveys of lab QC operations have been known to be perfunctory and reliant on assurances that what is contained in the QA manual is in faithful practice. Cases are known where the QA program goes little further than the QA manual. The manual must first be reviewed to determine that it provides all requisite QC operations. It must then be verified that the program is truly in effective use. This will be obvious by spot checking records, accuracy/precision charts (Shewhart or equivalent), notebooks, calibration tags and schedules, and so on and then by following a sample through the entire laboratory process.

SECTION 3.0

TEST PLAN

3.1 STATIONARY SOURCE TESTING

In the following discussions (Secs. 3.1.1 through 3.1.9), the nine categories of "hot spots" identified in Table 1-3 of the Introduction will be considered. In each case, the best or only possible site has been sought. The most practical sampling approach within cost constraints for each type facility and pollutant(s) of interest is then defined. Where very complex operations are involved, a sampling of only a fraction of the possible emission sources is called for, which will then require that the data obtained be extrapolated to a larger population of like sources within the facility. Similarly, extrapolations between like facilities will also be necessary, imposing the assumption that the type of processes involved and the process rates of these are the principal variables.

Because the level of site inspection and test plan development possible on the present program was limited in terms of the available funding, the test plan proposed here must be regarded as preliminary in nature. On implementation of this plan, or modifications thereof that develop through interim improvements, considerable further detailing will obviously still be required. This should be preceded by additional site visits not only to expand the test plan specifications but to update the information already provided. In most of the plants visited, activity in the improvement of APC capability was quite dynamic such that month-to-month changes in such systems should be expected.

3.1.1 Primary Steel Mill

A. Background--

Using an arbitrary hazard scaling formula, California's only integrated steel mill received the highest number of points of all the stationary sources considered. The pollutants included were arsenic, benzene, cadmium, and POM. The scaling factors of the two organic categories added to 95% of the total. This was about the same fraction as represented by the estimated mass emissions of the organics relative to the total of all four categories of materials. This is summarized from the following tabulation excerpted from the Task II Volume, Table 2-1:

Pollutant	Estimated Annual Emissions, Tons	Arbitrary Hazard, Scaling Factor, $\times 10^6$
Benzene	112	54.5
Cadmium	7.0	3.4
Arsenic	1.6	0.5
POM	27*	17.5

* Based on measurement of Benzo[a]pyrene (BAP) as POM surrogate and assumes POM/BAP ratio = 10

The emergence of the Kaiser steel mill as the most prominent "hot spot" in this arbitrary ranking procedure is not surprising. In November 1976, the CARB characterized the plant as "the largest single stationary source of visible and invisible air pollutants in the South Coast Air Basin" (Ref. 46). Kaiser has invested and continues to invest heavily of its resources to reduce emissions at the Fontana plant.

Operations at the Kaiser mill consist of the following elements:

- Four blast furnaces
- Three open hearth and five basic oxygen steel furnaces
- Ore sintering plant
- Seven batteries of coking ovens (315 units)
- Coke by-product plant

- Various Mills:
  - Plate (148 in.)
  - Hot strip (86 in.)
  - Universal slabbing
  - Blooming (46 in.)
  - Galvanized coil and sheet
  - Electric weld pipe
  - Tin plate
  - Cold sheet (60 in.)

As pointed out in the Task II Volume, the principal points of concern for emission of the four carcinogenic materials are as shown.

TABLE 3-1. TARGET POLLUTANTS ASSOCIATED WITH STEEL MILL OPERATIONS

Pollutant	Steel Mill Source	Estimated % of Total
Arsenic	Blast Furnaces & Other Foundry Operations	48
	Coking Operations	52
Cadmium	Coking Operations	100
Benzene	Coking Operations	100
POM	Coking Operations	99
	Sintering Plant	1

The above estimates are based on national practice wherein emission factors were generated from calculated and/or test data for both controlled and uncontrolled operations. In considering the individual sources, therefore, the level of control in place at Fontana and the inherent controllability of the process itself must be taken into account. The following discussions deal with these matters and are based on information provided by Kaiser Steel Corporation, the SCAQMD (Colton Office), previous and current KVB site visits, and informational sources referenced in the Task II Volume, Sections 3.1, 3.3, 3.4 and 3.11.

1. Blast furnace and foundry operations--The four blast furnaces at Kaiser are rated at a combined output capacity of 7825 tpd. All are single tap-hole in-line furnaces. Unit No. 4 has hard slag pits and open cast house floor that is not back filled to yard level. The Unit No. 4 slag pits are located adjacent to the cast house building with ladles spotted under a lean-to and under the main cast house floor. The other units have back-filled cast house floors with slag pits also located next to the cast house building but the ladles are located under lean-to roofs and in arcades under the main roofs. This discussion of cast house arrangements derives from the fact that the CARB cited visible emissions from the slag pits and slag tapping operation but not the blast furnace stacks themselves (Ref. 46).

The gases leaving the top of the blast furnaces, which are rich in carbon monoxide, are passed through purification trains and are then used to fire the blast furnaces and other furnaces in the plant. It is likely that any arsenic emitted from casting operations will be in fugitive processes. In cleaned stack gases from a cast house sampled by EPA contractors (Ref. 47) arsenic (or cadmium) was not found.

Analogous conditions exist in other operations that might mobilize arsenic from pig iron or steel. These include scarfing, pit soaking, remelting and related thermal processes that may not have air pollution control systems.

The iron-purification steel furnaces producing most of Kaiser's output are the five basic oxygen steel process (BOSP) units. Use of the open hearth furnaces is avoided now because of economic considerations. Of the original nine open hearths, only three are now operable and only two of these may be used simultaneously to be compliant with air pollution control regulations. Because the BOSP furnaces are able to charge less scrap than do the open hearth furnaces, Kaiser no longer purchases outside scrap. In fact, the internal supply from its own mills is now greater than is required for steel making. In any case, the absence of dealer scrap with its admixtures of cadmium plated objects suggests that the steel furnaces would not be found to emit significant amounts of cadmium. This is the only one of the four pollutants (with arsenic, benzene and POM) associated with the steel furnaces (see Sec. 3.4 of the Task II Volume). Cadmium is, however, found in coke oven effluents as are the other three pollutants.

2. Coking operations--The principal sources of airborne emissions from closed coking ovens are the top coal-charging ports (3 per oven), the risers (2 per oven) ducting off coke gas to the oven mains which terminate at the coke by-product recovery plant, the larry cars (while charging ovens), and the seals of the doors on either side of each oven. When the oven doors are opened, additional emissions are seen when the charge is pushed from the oven into the quench car. The contents of this vehicle release emissions even after being quenched with water, which process is accompanied by further airborne releases (besides steam).

The coke by-product plant employs a direct primary cooler, ammonia absorber, and final cooker (tar-bottom water contact type). The gas is not now desulfurized but a desulfurization unit is under construction. Recovery of benzene-rich oil was scheduled to be discontinued as of November 24, 1979. This fraction will be maintained in the coke gas stream which fires some of the coke ovens. Blast furnace gas, carbon monoxide being the principal fuel constituent, is also used except in batteries A, B and C. The other batteries can fire either coke oven gas, blast furnace gas, or mixtures thereof.

Combustion gas from the under-fired coke oven burners is relatively clean itself. As it passes up through the refractory ducts which heat the contents of adjacent coke ovens, it becomes contaminated by smoke and vapor leaking through the wall from the oven to the combustion flue. Four of the batteries (B, C, D & E) are now equipped with bag houses. Additional bag houses are under construction to clean the combustion gas from the other units. Batteries F and G were to have been on stream with their new bag houses by December 1979 and Battery A by March 1980.

The seven batteries (45 ovens each) at Kaiser incorporate various door designs. Batteries A and B have bottom hung doors. This design is characterized as most prone to leakage (Ref. 48). The balance of the batteries are fitted with top hung doors. Five of the batteries employ cam latches on the doors while batteries F and G are screw latched. Battery E and Battery D have just undergone an extensive overhaul.

The air pollution rating of the Kaiser coking ovens has improved considerably since November 1976 when CARB visited the plant and issued a number of citations (Ref. 46).

Oven top leakage has been reduced through the substitution of a clay luting compound (sealant) for coal dust as well as improved operating practices. Operation of the Kaiser larry cars is in conformance with CARB's recommended techniques for staged coal charging from modified design larry cars.

Door seals are maintained on a continuing basis but, because of their greater linear run, are the source of more citations than are luted top fittings. Kaiser attempted door luting for awhile. They found that it led to greater warpage (and consequent leakage) than the traditional effect of allowing tarring coal in the charge to seal the knife edge.

The SCAQMD has estimated particulate emissions from the Kaiser coking batteries for 1979 as shown in Table 3-2.

TABLE 3-2. COMPUTED KAISER STEEL CORP. COKE OVEN FUGITIVE EMISSIONS USING CURRENT SCAQMD EMISSION FEE FACTORS*

Source	Emission Factor, Lb Particulates/ Ton Coal Charged	Particulate Pollutants, Tons/Yr
Door & Topside Leaks	0.041	39
Charging	0.050	47
Pushing	0.609	577
Quenching	0.076	72
	Total	735

* Based on predicted coal charging of 1,893,333 tons in 1979.

This represents a considerable reduction over the emission factors used in 1977 by the AQMD. At that time the total for the seven batteries added to 1890 tpy. The reduction of course has resulted from the many improvements in the operation that Kaiser has introduced.

Meteorology Research Inc. (MRI) performed some testing for Kaiser to determine the particulate emissions from one door on battery A (Ref. 49). They showed that the mass release is greatest following charging and then drops about two orders of magnitude over the ensuing first two hours of coking. Unfortunately, MRI was unable to measure emissions during the first 30 minutes following charging because the nephelometer used went off scale. A maximum release rate of 0.4 lbs/hr was reported by MRI, which apparently is an extrapolation. Using this rate at zero time and modifying the MRI log-log curve plotting mass release vs light scattering to incorporate a linear time based abscissa, one can integrate an emission factor from the measurement. This proved to be 0.30 lb/charge. Assuming 14.2 tons of coal per charge, the doors on all seven batteries would release 20.0 tpy of particulates in 1979. It should be emphasized that this study was conducted on one of Kaiser's oldest batteries and involved only one door and required extensive data extrapolation.

In 1976, KVB sampled the stacks of coke batteries C and D (the latter since refurbished). The material of interest was volatile hydrocarbons (Ref. 50). Total organic emissions were computed at 381.4 and 172.9 tpy, respectively. The compositions of the Battery C and D gases shown in Table 3-3 vary considerably (6.8 and 74.3 tpy, respectively) with respect to benzene. The fact that Battery D, which fires predominantly blast furnace gas (essentially devoid of benzene), produced the largest release of benzene accents the observation made earlier that separation of the oven vapors from the combustion flue gases can be poor.

3. Ore sintering plant--The function of the sintering plant is to convert various fine iron-bearing materials into aggregates that can be charged into the blast furnace with the coarser iron ore. This agglomeration is produced by high temperature roasting on grates in the presence of crushed coke and fluxing material (limestone). The coke is ignited and partially reduces the iron-bearing materials which, being in a semi-molten state, coalesce to form larger, semi-porous sinter.

A continuous sintering process is shown in Figure 3-1. A traveling grate conveys a bed of ore fines, or other finely divided iron-bearing material, intimately mixed with approximately 5% of a finely divided coke. Near the head or feed end of the grate, the bed is ignited on the surface by gas burners and, as the mixture moves along the traveling grate, air is pulled down through the mixture to burn the fuel by downdraft combustion. As the grate moves continuously over the wind boxes toward the discharge end of the strand, the combustion front in the bed moves progressively downward. This creates sufficient heat and temperature (1313-1480 °C; 2400-2700 °F) to sinter the fine ore particles together into porous coherent lumps. Flux can be added in the feed mix to eliminate flux charging partially or completely in the subsequent ironmaking operations. The flexibility of the process permits conversion of a variety of materials, including naturally fine ores, ore fines from screening operations, flue dust, ore concentrates, and other iron-bearing materials of very small particle size.

TABLE 3-3. VOLATILE ORGANIC STACK GAS EMISSIONS FROM UNDER-FIRED COKE OVENS

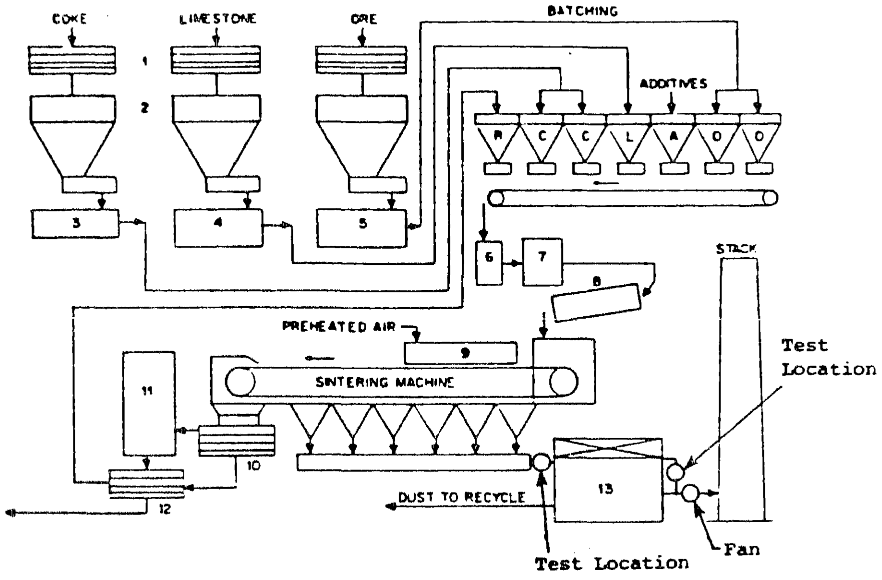
Source: Ref. 50

	Battery C*		Battery D†	
Constitutent	Wt. %	Tpy	Wt. %	Tpy
Methane	82.8	316	41.0	70.8
Ethane	2.5	9.5	1.4	2.4
Ethylene	11.7	44.6	2.8	4.8
Propylene	0.3	1.3	5.5	9.5
Acetylene	0.8	3.2	--	--
Butylene	--	--	6.4	11.1
Benzene	1.9	6.8	43.0	74.3
Total	100.0	381.4	100.0	172.9

* Fuel Gas: 2500 acfm coke oven gas

† Fuel Gas: 13,333 acfm blast furnace gas + 83 acfm coke oven gas

At the Kaiser plant two strands are operated having a total capacity of about 2500 tpd. Air cleaning equipment (bag houses) has been in place since 1971 to handle the combustion gases of the plant.



A = Additives
C = Coke fines
L = Limestone fines
O = Ore fines
R = Return fines

1. Raw-material screens
2. Raw-material storage hoppers
3. Rod mill to reduce size of coke
4. Limestone crusher
5. Ore crusher
6. Mixing drum
7. Raw-sinter mixer
8. Rerolling drum
9. Burner hood
10. Sinter screening (hot)
11. Sinter cooler
12. Sinter screening (cold)
13. Baghouse

Figure 3-1. Typical iron ore sintering process.

Production of POM during sintering is occasioned by the combustion of coke. Because the coke has been depleted of most of its organic matter, yields are lower during sintering than in coking (see Table 3-1).

B. Site Visit--

The Kaiser plant has been sampled by KVB personnel on two previous programs under CARB contract (Refs. 50 and 51) and on other occasions while under retainer to Kaiser. Because of the considerable recent activity at the Fontana plant in the installation of APC equipment, an updating was considered desirable. The Kaiser environmental office permitted this and a plant tour was conducted on September 19, 1979. At the same time, Kaiser indicated willingness to cooperate in source testing at their plant provided it was properly designed. A general plant plan was provided with no proprietary restrictions being stipulated.

The tour of the plant did show an impressive amount of activity in air pollution abatement. Of particular note was the new BOSP plant. This structure is entirely enclosed and, aside from a small steam plume from a top vent, evidenced no visible emissions at any point. The recently installed metal desulfurization system was in operation. While the molten contents of torpedo cars are lanced, particulate emissions are collected in an overhead duct-work and are cleaned in a bag house. The various other APC systems in operation or under construction that were mentioned in the preceding section were also seen. In terms of visible emissions, the principal sources observed were random leaks from coke oven doors, the east-end quenching tower, and short-term smoke releases from various stacks.

When visited, all of the open hearth furnaces were off-line; six of the coking batteries were operating with refurbished Battery D scheduled to go back in service that night (September 19, 1979).

C. Sampling Approach--

1. Wind and background influence--Because of the close proximity of the sources under investigation, precautions must be taken to assure that the wind direction does not cause intermixing of the effluents. Further, sampling during periods of wind direction other than westerly could cause sample influence by other local industries. An adequate upwind station is in operation by the Kaiser environmental department which is situated west of all mill operations. Simultaneous ambient samples can be taken within the mill and the various stations described below if correction for upwind values is not otherwise provided.

2. Coking ovens--Excluding the possible presence of other arsenic sources, the principal focus will be on coking operations. With the exception of the coke oven combustion (burner) flue gas stacks, emissions from the coking ovens are fugitive. The best approach for determining the content of these emissions in terms of the four classes of materials is by area sampling. By determining the composition of the TSP caught, the release of arsenic, POM (or surrogate), and cadmium can be calculated from best available emission factors for TSP. The EPA is reviewing data submitted by Midwest Research Institute on the iron and steel industry which will be incorporated in their AP-42 by revision. A copy of these emission factors was furnished KVB but cannot be quoted at the present time because of the draft status of the report.

Alignment of the ovens is about on the prevailing wind (westerly) with the by-product plant just to the north of this line and the four blast furnaces aligned parallel to the south (see Figure 3-2). Separation of the batteries from the by-products plant is probably adequate if the wind does not trend into the southeast quadrant. Fugitive emissions from the cast houses and slag pits would occur at the south ends of each of the blast furnaces, or about 350 ft. from the outer line of the coke oven batteries. Due west (upwind) of the coking ovens, the only hot process is the sintering plant. This is almost 1000 ft from the nearest coking battery and vents most emissions from a tall stack.

The principal concern of major intersource contamination is the quenching towers. These are almost in-line with the coking batteries, with one situated on either end and one between batteries E and F near the east end.

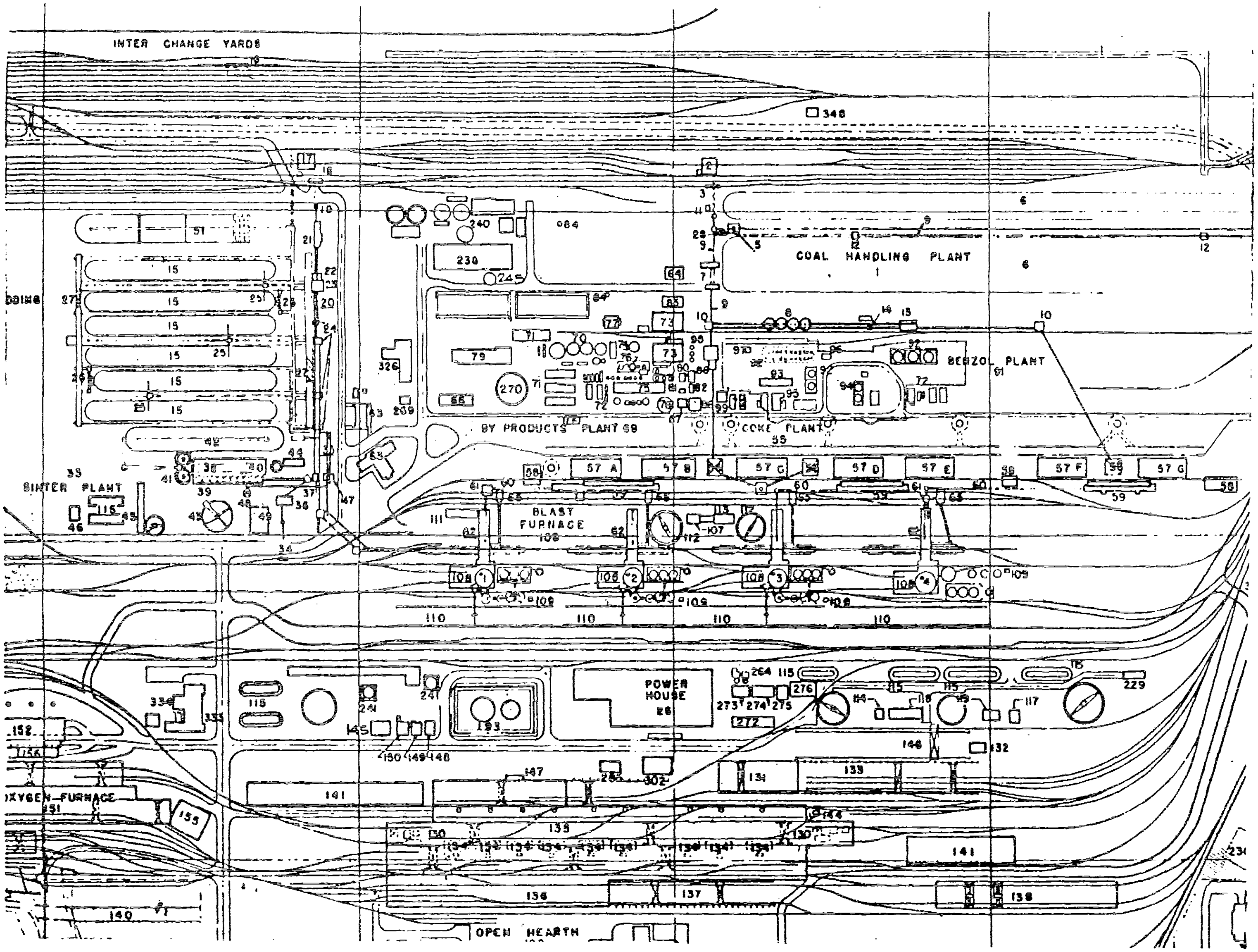


Figure 3-2. Kaiser steel mill: General plan of northeast portion of plant.

Because the emissions from the coking batteries will be much richer in the materials of interest than those from the quenching tower, mixing in of quenching tower emissions should be avoided. This will best be done by sampling between battery E and the quenching tower east of it about 150 ft. This would avoid emissions from two of the quenching towers (on a westerly wind) while situating the sampler almost 1500 ft downwind of the west-end tower. Emissions from the coke wharves cannot be avoided but these should be minor so long as the piles do not ignite.

Because sampling will be done at some distance from the nearest oven, it can be assumed that all of the cadmium and arsenic and most of the higher boiling POM reaching the sampler will be predominantly in the condensed phase. Therefore, these constituents may be determined from the catches on a high volume filter such as the Stapler Air Sampler. Several runs of at least four hours duration each should be made. Collection of benzene should be done simultaneously using a lung-type bag sampler set at a low fill rate. Time-integrated sampling over at least one hour should be done. From the high volume sampler, TSP/M^3 will be determined and in the Tedlar bag, benzene content per M^3 will be determined. Thus, for the period sampled, the amount of benzene released for a unit weight of TSP is known and can be multiplied by the fugitive TSP emission factor to determine fugitive benzene release for the entire battery.

After weighing the filter catch from the high volume sampler a small measured section will be removed for the determination of arsenic and cadmium. The balance of the filter will be extracted to furnish a POM solution for analysis.

3. Quenching towers--One of three towers should be sampled for particulates. Considering the nature of the coking process, the presence of benzene constituents in any significant amount in the quench plume is not likely. Obtaining samples from the top of a quenching tower is quite dangerous. The releases issuing from the tower quench car portals probably have the same composition as those leaving the top of the tower, except that considerably less steam is incorporated.

Given a westerly wind, the best sampling site will be the tower to the west of Battery A. Here coking oven emissions should not contaminate the catch. Sampling can again be done using a high volume sampler. The device should be set up fairly close to the tower since the updraft caused by quenching tends to pull the fugitive portal emissions directly upward. TSP will be measured and, from the compositional analysis of the catch, release rates for cadmium, arsenic and POM (or surrogate) calculated using appropriate emission factors.

4. Coke oven stacks--Because all batteries will be equipped with bag houses within a year or so, sampling should be performed on a stack releasing cleaned flue gas. Batteries B, C, D and E are therefore suitable. Also, combustion gas from burners fueled with coke oven gas and predominantly blast furnace gas should be considered. Battery B is a case of the former fueling while Batteries D and E usually fall in the latter category.

Primary interest will be in the measurement of benzene content, since the APC equipment has no effect in reducing levels of that pollutant in the released stack gases. Unlike the area sampling discussed in the preceding subsections, reliance on emission factors will not be necessary for this stack testing, if properly performed.

Sampling of the two selected stacks should be done using the standard EPA Method 5 approach with distilled water loaded into the first two impingers. It is doubtful if much volatile arsenic (or cadmium) will be present to enter the impingers, but some fine particulates which will dominate in the solid phase material surely will. A 0.4 µm pore-size filter, by definition, does not stop all of the solids. As with the high volume area samples, the catch should be tested for the two metals and POM. In the latter case, analysis for POM individuals or surrogate (BaP) should not be pursued if the BSP* weight is too low to justify analysis.

Benzene sampling at the stacks should be conducted in parallel with the Method 5 work, so that the flow rates will be known. Use of parallel (replicate) solid adsorbents is considered the best approach. Bagging may not be suitable because of wall losses from the comparatively organic-rich flue gas. Glass-tube grab samples are contraindicated because of the possible periodic changes in gas composition that could be occasioned as ovens are pushed and charged.

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* Benzene Soluble Particulates

Because of the probable plentiful catch of benzene, its comparatively high vapor pressure and the temperature of the flue, the adsorbent of choice is charcoal. Jumbo-sized personal sampler tubes can be used in a train fitted with critical orifices, air flow meters, and a single gas pump. Sampling over 30 minutes to an hour will be appropriate. If breakthrough appears possible, capacity of each replicate can be doubled by using two or more tubes in series. Recovery of benzene would be done in a manner analogous to NIOSH P&CAM 127, using carbon disulfide as solvent. Recovery and blank testing will be critical. Benzene recoveries from charcoal can be as low as 80%, and charcoal blanks almost always exhibit impurities of light aromatics.

In the analysis of the tubes, the extracts may also be tested for the presence of lower molecular weight POM, particularly naphthalene. These compounds may not be entirely retained on the stack-temperature filters and, unless POM surrogate analysis is being done, should be expected in both the solid and vapor phases of the flue gases.

5. Coke by-product plant--Kaiser will abandon the recovery of coke light oil (50-60% benzene) because, as they state, of the economic impact of SCAQMD Rules 462 and 463 (organic loading and storage). This situation is fluid, however, and the burning of the vaporized light oil (with coke oven gas) in the coke oven furnaces is uncertain as a fixed practice. For the purpose of the present report, it will be assumed that storage of light oil will no longer be done. Because of this process change, the characteristics of the final cooler cooling tower are uncertain. This device has been identified in a recent EPA testing program (Ref. 52) aimed at coke by-products plants as the single greatest emission source in benzol plants. In terms of by-products plant benzene emissions, 52% occur at the final cooler cooling tower, 22% at the tar decanter, 9% at the primary cooler condensate tanks, and 17% from the light oil storage tank, according to that report. Due to rounding, these fractions add to 100%, although other minor sources are identified. The final cooler cooling tower and the tar decanter are also designated as being reponsible for 94% of the POM emissions in the coke by-products plant. The proportions are about 60/40 for the two sources, respectively.

Thus, if light oil storage is omitted, testing of three source types should be sufficient to characterize the coke by-products plant in terms of benzene and POM.

Assuming that the final cooler cooling tower is operating, samples can be taken from the air stream directly above the cooler. Because flow rate would be difficult to measure in this structure, design rate should be used, if available. Collection of the organic species should be done using separate collectors for POM and benzene. Because the air temperature in the cooler will be only slightly warmer than ambient, a polymeric adsorbent, such as Tenax, can be used. Charcoal would also be satisfactory, if the precautions noted earlier in this subsection are observed.

Collection of POM can be done isokinetically using a train consisting of a filter and an extractable adsorbent such as XAD-2. The latter is necessary, since considerable vapor phase (e.g., naphthalene) POM will likely be present.

The same procedures can be used in sampling the tar decanter vents. These ducts move gases at fairly slow flow rates, and will have to be individually checked with an anemometer to identify the best sampling point(s) Extrapolation of the results obtained for one or two vents to the total flow represented by all of the ducts venting the decanter tanks can then be done.

Sampling the primary cooler condensate tank(s) involves a fairly slow updraft of warm gas containing significant amounts of benzene. Effluent rate can be determined using an anemometer and benzene composition by the analysis of several grab samples. Time integrated sampling does not appear necessary since emissions from these sources should occur at fairly constant rates.

6. Blast furnaces--As pointed out earlier, arsenic and cadmium emissions from blast furnaces probably occur as fugitive effects from the cast houses and slag pits. Thus, area sampling (2 to 4 hours) is indicated.

Because the air path will have caused condensation of any volatile forms of these metals or their salts to occur, filter sampling should be acceptable. After the TSP of the catch is gravimetrically measured, then the fractional amounts of the two metals in the TSP will be determined. Total TSP released as fugitive emissions will have to be estimated from data obtained from other steel mill casthouse fugitive fume collecting devices. Reference 47 provides such information.

The most favorable point for the positioning of a high volume sampler will be blast furnace No. 1, between the blast furnace gas stoves and the rail spur to their south.

7. Sintering plant--Control of emissions from the sintering plant is accomplished by a bag house system. Because the amount of POM emissions attributed to the sintering plant is minor with respect to other operations (see Table 3-1), testing of this facility may be regarded as optional. If pursued, however, bag house effluent should be sampled (isokinetically) using a Method 5 train. In lieu of impingers, the filter should be backed up with an air adsorption tube packed with XAD-2.

8. Other possible test sites--Other plant operations that may warrant attention are the coal storage piles, open hearth furnace ESP stack and roof emissions (if furnaces are in use) and the plate mill and hot strip mill stacks. All of these points were identified by CARB (Ref. 46) as being sources of occasional or intermittent releases. Because these sources are not well characterized with respect to the materials of interest, it may be worthwhile to collect TSP samples for compositional analyses. Nonisokinetic sampling with a simple filter train should serve for this purpose.

9. Test plant summary--The various tests proposed for the Kaiser Steel plant are summarized in Table 3-4.

10. Test scheduling--A number of SCAQMD rules contain firm compliance dates that Kaiser intends to meet. Fulfillment of these rules will have a definite impact on the results of implementing the present test plan. It may therefore be advisable to consider scheduling of the individual test plan operations so that the plant units affected by the compliance program at Kaiser will not be tested until after such compliance has occurred. The existing rules with compliance dates are as follows:

TABLE 3-4. SUMMARY OF POLLUTANT TESTING OPERATIONS PROPOSED FOR THE KAISER STEEL PLANT, FONTANA

Site	Test Materials Sought	Method of Sampling	Derivation of Annual Pollutant Emission Rate
1. Coking Ovens (all)	All	Area Sampling: (a) Particulates: Hi-vol Filter (b) Volatiles: Tedlar lung	(a) Particulates = E.F. (TSP) X Annual Process Rate X TSP Wt. Frac. (As Cd, POM) (b) Volatiles = $\frac{\text{Wt./SV X Ann. Proc. Rate X E.F.(TSP)}}{\text{TSP/SV}}$
2. Quenching Tower (1)	As, Cd, POM	Same as 1 (a)	Same as 1 (a)
3. Coke Oven Stacks (2)	All	In-Stack Sampling: (a) Particulates: Method 5 (b) Volatiles: Charcoal Tubes	(a) or (b) $\overline{\text{wt}}$/SV X SFGV/hr x $\frac{\text{Ann. Proc. Rate}}{\text{Avg. Hrly. Batt. Rate}}$
4. Coke By Product Plant (a) Final Cooler Cooling Tower (1)	POM, Benzene	In-Tower Sampling: (a) POM: Filter + XAD-2 (b) Benzene: Tenax or charcoal	(a)or (b) Wt/SV X design SV/hr x hrs/yrs on stream
(b) Tar Decanter Vents (I or 2)	POM, Benzene	From Attached Flex. Duct Same as 3	Wt/SV X ΣSFGV/hr X hrs/yr Operating
(c) Primary Cooler Condensate Tank (1)	Benzene	Several Grab Samples	Wt/SV X SFGV/hr x hrs/yr Operating
5. Blast Furnaces (1)			
Cast House & Slag Pit	As & Cd	Method 5	Same as 3
6. Sintering Plant Older Bag House Stack (Discretionary)	POM	Method 5 + XAD-2	Same as 4(c)
7. Upwind Station	All	Same as 1(a) & 1(b)	Same as 1(a) & 1(b)

Terms:

E.F. = Emission factor per latest revision of AP-42

TSP = Total suspended particulates

SV = Standard volume in common units

SFGV = Standard flue gas volume

Method 5 = EPA-approved particulate sampling technique (Federal Register Vol. 42, No. 160, Thursday, 8-18-77

Regulation	Subject	Compliance Date
SCAQMD 462 & 463	Organic Liquid Loading & Storage	January 1980
EPA Decree	Coke Oven Gas Desulfurization	April 1980
SCAQMD 464	Oil-Effluent Water Separator	June 1980
SCAQMD 477	Coke Oven Door Seals	June 1980
SCAQMD 477	Battery A Rehabilitation	June 1980
SCAQMD 477	Battery B Rehabilitation	January 1981
SCAQMD 477	Coke Pushing Control- First Phase	January 1981

3.1.2 Refinery Operations

A. Background--

In Task II discussion on benzene (Sec. 2.4 of that volume), the emission of benzene is predominantly associated with the automobile. In the following Special Testing Section, paragraph 3.2, which deals with recommended testing of non-stationary sources, this fact is stressed.

Although large stationary sources are estimated to release only a small fraction of the benzene found in ambient California air, the amounts nonetheless prompt attention. These data* are tabulated below.

ESTIMATED BENZENE EMISSIONS FROM
STATIONARY SOURCES IN CALIFORNIA

Operator	Location	Est. Benzene Emissions, tpy
Kaiser Steel Corp.	Fontana	112
Chevron USA	Richmond	50
Chevron USA	El Segundo	30
ARCO	Carson	25
WITCO Chemical	Carson	14

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* See Task II Volume: Section 3.3.7

The Kaiser steel mill was separately addressed in the last section so that attention focuses on the above tabulated refineries. The WITCO Chemical Co. operation was of least interest because the processing of benzene to produce alkylated detergent represents a far simpler operation than that of a refinery. Much of the stock flowing in refineries contains some or considerable percentages of benzene. These stocks are involved in a variety of processes, comprising a very complex system. The Chevron refinery at El Segundo emerged as of particular interest because, in addition to its large scale activities in producing most conventional refinery items, the refinery produces industrial benzene and converts part of it to cumene (isopropylbenzene). The ARCO refinery also produces industrial benzene but does not consume any internally. Chevron Richmond and WITCO both convert benzene to alkylated detergent (dodecylbenzenesulfonic acid).

Contact was made with both Chevron, El Segundo, and ARCO, Carson. When the former company expressed willingness to participate in the test plan, if it were adequately designed, focus was shifted to that refinery.

Chevron furnished the project considerable information, thus simplifying the test planning effort a great deal. Due to the proprietary nature of some of the material, we were asked to treat the information as confidential. It will, therefore, not be reproduced in this report. Also, discussion here of the refinery's processing systems will have been reviewed by Chevron for any sensitive content.

Included in the data submitted by Chevron was a general plant layout, hand color-coded to show process streams containing benzene at three different levels (<2.0; 2.0 - 10; >10 Vol %). Also supplied were similarly color-coded process diagrams of those units in which benzene-rich streams were produced or handled. These included:

- Aromatics recovery plant - distillation and extraction sections
- Cumene plant
- Aromatics Rheniformer unit
- Catalytic cracking unit - distillation section
- No. 2 naphtha hydrotreater
- Gasoline fractionating unit

Additionally, lists of pumps covered by SCAQMD Rule 466* were supplied for three of the above units plus the coker plant. Pump lists for other units of interest will be supplied on request. Also available is Chevron's inventory of "Rule 466" valves. This includes some 33,600 valves all of which are segregated into the various process units which they serve.

The benzene operations begin at the Rheniforming (name derives from the catalyst which incorporates rhenium and platinum) unit. Naphthenic stock, which is rich in cyclohexane and alkylcyclohexanes, is dehydrogenated to yield corresponding aromatic structures. This output is then distilled and the benzene fraction is fed to an extraction unit which preferentially accumulates the benzene in phenol and sends back undesired naphthenic/paraffinic material. The benzene rich solvent is passed through a stripper, from which the phenol is recycled.

A portion of the benzene production is used for cumene manufacture. This involves the combination of benzene with propylene in a fixed catalyst reactor. The reaction products are stripped of light ends and then distilled to yield cumene, the benzene fraction recovered being recycled in the reactor.

Benzene storage is managed in five floating-roof tanks, two serving the cumene plant, one the marine terminal, and the other two the aromatic recovery plant (for further transfer). Shipment of benzene is essentially all done by ocean tanker. Loading is from an on-shore pump house through underwater piping to an offshore tanker mooring.

B. Site Visit--

Two tours of the refinery were made. The first was conducted on September 25, 1979 and the second on October 2, 1979. The Chevron guide showed the entire refinery on the first visit, while the second tour was restricted to the aromatics recovery plant, the aromatics Rheniformer unit and the catalytic cracking unit. Inspection of the cumene plant could not be carried out because of an on-going maintenance problem there.

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* Rule 466 requires pumps and compressors handling organic materials having Reid vapor pressures >80 Torr to have mechanical seals in good working order. Inspection requirements and leakage limits are specified.

Because of the highly complex nature of the refinery and the basic test approach that had already been decided upon, the principal purpose of the site visit was to ascertain the general accessibility of the testing points. With the exception of components mounted on high vertical shapes (distillation columns, reactors, etc.), no serious access problems were noted. Another fact favoring test work was that the operators had conspicuously tagged hydrocarbon service pumps. Also, valves that had exhibited previous leakage were red-tagged as "leakers" even though repaired. Chevron personnel safety precautions were also discussed.

C. Sampling Approach--

1. Basic methodology--Because of the complexity of even a small refinery, determination of a single chemical emission rate for an entire refinery using measurements that are inclusive of all release paths would be prohibitively expensive. A far more practical approach will be to determine for the various type release sources the average concentration of benzene, then apply these percentages to the total hydrocarbon emissions that have been determined for such sources in previous surveys (Ref. 53).

An exception to this approach will be fugitive leakage from valves, pumps and compressors. Because of the application of SCAQMD Rule 466, Chevron has doubtless reduced the incidence of hydrocarbon leakage from such hardware to levels perhaps considerably lower than those imputed by AP-42 or measured by the CARB (Ref. 54). Therefore, actual rates of benzene escaping from a representative population of such devices should be measured.

As a result of their experience in testing valves, pumps and compressors at thirteen refineries, Radian Corp. has published (Ref. 55) nomographs relating valve and flange leakage rate to THC readouts. The procedure is limited to vapor/gas streams, which is not a serious drawback since these lines were found to leak off considerably more hydrocarbon than liquid service systems. Using a Bacharach TLV sniffer, four readings are taken around the likely leakage source. The highest reading is then graphically related to mass release within confidence limits which involve reasonable error bands provided an adequate population of hardware is tested. This approach permits the testing of a large number of valves and flanges such that any argument as to the statistical adequacy of the actual subset sampled is precluded.

In order, however, to establish the percentage of benzene in fugitive releases, it will also be necessary to sample the emitted vapors and determine their compositions. This can best be done by valve-bagging techniques, such as those described in References 50 and 53, and collecting the vapors in Tenax adsorbent or in Tedlar sample bags. The contents of these catches would then be analyzed by GC to determine the mol-fraction of benzene in the organic moiety.

2. Scope of survey--In selecting the test areas to be sampled, there will be no point in considering stocks and streams in which benzene should be absent or present at only negligible levels. The color-coded refinery layout furnished by Chevron will serve as an excellent guide for this purpose. It should, however, be reviewed with Chevron engineers to insure that possible other benzene sources had not been overlooked.

Once the areas of test interest are mapped, the detailed test plan will be segregated into subtasks comprised of specific unit processes. As identified by Chevron, these would include the following:

- Distillation and gas recovery plant
- Steam naphtha reformer unit
- Catalytic reformer units
- Naphtha hydrotreater unit
- Cumene plant
- Jet hydrofiner unit
- Crude units
- Rheniformer plant
- Aromatic recovery plant
- Catalytic cracking plant
- Coker plant
- Caustic treating plant
- LPG plant
- Filling plant
- Gasoline fractionation unit
- Gasoline blending

This breakdown of process units would be supplemented by (1) storage facilities holding benzene, gasolines, crudes and other benzene-containing stocks; (2) the off-shore cargo transfer; and (3) API water/oil separators.

3. Process unit sampling--Each process unit will be studied and the expected "aromatic" portions identified. In the cases of streams or flue gases that are of uncertain composition, analytical data previously obtained by KVB at other refineries can be used (Refs. 50 and 56). For example, the flue gas from the fluid catalytic cracking (FCC) unit is fired in a carbon monoxide boiler equipped with an electrostatic precipitator. The effluent of the latter is said by AP-42 to release 220 lbs of hydrocarbons for every 10^3 bbls of oil input to the FCC unit. At the ARCO refinery, KVB found considerably lower THC levels in the CO boiler effluent which, on GC speciation, showed no evidence of benzene (Ref. 56). In other cases, the amount of benzene in a stream may be uncertain such that the testing of any fittings or devices in that portion of the system might prove a poor investment of labor. In such cases, the stream should be sampled and tested for benzene on site. This can be done using a Century OVA Analyzer equipped with a tri-column GC option and isothermal field column oven. Either gaseous or liquid (preferably diluted with CS_2) samples can thus be run.

Once the "aromatic" streams have been identified for each process unit, an approximate valve and flange inventory of that section will be developed. This will hopefully be possible in part using the Chevron Rule 466 valve inventory described earlier. The flange (other than valve flanges) population can be estimated from pipe-run lengths. Following this count and depending on its magnitude, from 5 to 10% of the fittings that are readily accessible and a lesser number of fittings that are accessible with effort but not in restricted areas will be checked with the TLV Sniffer. For gas/vapor service valves and flanges, the mass leak rate, if any, can be immediately logged using the Radian nomographs. Leaking fittings in liquid lines will be logged by the TLV readout only, which value will afford at least ROM sizing of hydrocarbon escape rate. All leakers will be tagged and plotted on process flow schematics. Selected leakers in gas/vapor-service will then be designated as being representative of the various streams having differing compositions. If the incidence of leakers permits, replicate valves and/or flanges in the same lines will be designated for further testing. Those gas/vapor-service leakers selected will then be bagged and a time-integrated sample of the issuing hydrocarbons collected. In the case of liquid service lines, the fittings will be bagged and purged into a THC analyzer to determine leakage rate. If the valve is actually dripping, a liquid sample will be collected; otherwise, a conventional Tedlar bag or Tenax tube sample will be collected from the purge stream. The mol-fraction of benzene in the hydrocarbon catches will be determined and multiplied by the THC mass release rates logged for the fitting tested and all those leakers flowing similar compositions of hydrocarbons. By extrapolation total fugitive benzene releases for all valves and flanges for each process unit will be determined. An exception will be the discharge piping on relief and safety valves. These lines are vented to vapor recovery and/or waste-gas flares.

Selected testing of aromatic-stream pumps and any compressors that might contain benzene* will also be similarly approached. The TLC sniffer will be used and where significant leakage from pump mechanical seals is detected, the device will be bagged to measure THC leakage rate and to collect a sample for determination of benzene fraction in the THC. Also, the liquid flowing into the process drain from the pans of selected pumps should be checked for benzene emissions. This will likely be considerably greater than that which is emitted from the drains. This emission rate can be measured by determining the benzene content in the outflow versus that in the emulsion leaving the shaft seal. The rate of flow of the latter would also have to be determined using a stopwatch and graduated cylinder.

Other devices that are allowed to drain into the API sewer system should also be checked if the wastewater is suspected of being contaminated with aromatic stock. Measurement of cooling tower emissions is an inadequate art and probably involves minor hydrocarbon flows. A possible approach would be to analyze the warm input water for purgable organics using the Bellar and Lichtenberg technique (Ref. 57). The mol-fraction of benzene in the

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* Limited test results (Ref. 51 and 56) do not suggest the presence of boilers as high as benzene in compressor streams.

volatile fraction can then be assumed to correspond to vapors released in the tower. This percentage could therefore be applied to the product of the AP-42 hydrocarbon emission factor (6 lbs/10^6 gal cooling water) and tower input rate to furnish benzene emissions.

Combustor stacks (e.g., boiler and process heaters) have been shown to contain negligible amounts of benzene in the hydrocarbon fraction emitted (Ref. 51). The same is true of exhaust gases from IC engines (Ref. 58). Blowdown systems, vacuum jets, atmospheric vents, safety and relief valve discharge piping and related equipment have all been tied into APC systems. The latter consist of vapor recovery installations and/or smokeless flares. Hydrocarbon releases from such equipment are considered to be negligible (Ref. 58).

4. Storage tanks--Emissions from storage tanks containing benzene and benzene-containing liquids will be calculated using new API formulae. These are currently under various review and will be released. Chevron identified some 35 tanks at its El Segundo refinery as containing either pure benzene or petroleum fractions and products that contain some benzene. All but one are of the floating roof type. These will be inventoried and grouped by fluid contents. Tank parameters (diameter, roof type, paint color and seal configuration) will probably be available from Chevron. Average wind velocity will probably also be available from Chevron or, certainly, the Weather Service. Vapor pressure of the contents will be on record at Chevron, or can be adequately estimated from AP-42 tabulations and nomographs. The only information that will be lacking will be the molecular weight of the vapor in the head space and the mol-fraction of benzene in this vapor. In the case of benzene stocks, these values need not be measured in the laboratory. For other petroleum liquids, samples of the head-space gas will be taken (from the tank vent or thief hole) for GC analysis. One or two tanks from each group storing similar stocks should suffice for this purpose.

5. API water/oil separators--The present methodology for measuring hydrocarbon emissions from covered API water/oil separators is considered inadequate by the EPA. One technique used (Ref. 53) multiplies the loss of residual volatiles in the input/output streams times slop oil rate. To

this is added the product of the volatile organic fraction in the water stream times wastewater rate. These volatile fractions are estimated, respectively, from pan evaporation (2ml layer over 8 hr period at room temperature) and by the Bellar and Lichtenberg technique mentioned earlier. The results have shown great scatter according to the EPA (Dr. B. A. Tichenor), and improved methodology is now being developed under their sponsorship. This work is being done at Engineering Science, Inc. The technique, which will be applied at ten refineries, is the Virtual Source Method, a meteorological multi-station technique requiring upwind-downwind THC measurements. Precisions from 8 to 20% have been obtained by this technique when separators are operating under reasonably steady conditions. Assuming that the ongoing study eventuates in a generally acceptable approach, its use at Chevron may be considered. Again, however, the mol-fraction of benzene in the "plume" would have to be determined. This can be done by taking a close-in sample on Tenax tubes and analyzing the thermally desorbed hydrocarbons by G.C.

6. Off-shore tanker operations--Chevron operates four buoy moorages at positions from 1/2 to 1-3/4 miles off the shore of the El Segundo plant. Essentially all of the benzene shipped out of the refinery is pumped into Chevron fleet tankers for delivery to the Chevron USA Richmond refinery. Other petroleum products are loaded at this moorage and crudes are off-loaded from Indonesia, Alaska and other sources. Hydrocarbon emissions, if any, should differ considerably depending on whether the ships are loading or off-loading, the vapor pressure of the cargo, the tanker design, vents (e.g., inclusion of vapor recovery equipment), and the incidence, if any, of spills while making and breaking connections.

As in the case of the on-shore tankage, the practical approach will be to estimate benzene releases from marine cargo transfer by using emission factors developed specifically for such operations. Work is currently underway at the Scott Research Laboratories, San Bernardino, to produce such factors based on actual on-board sampling at the ARCO moorage. In order to apply such factors, further knowledge of the nature of the Chevron tanker traffic will be necessary and the role of the benzene partial pressure in the various products moving between ships and shore.

If at-sea sampling is done, benzene concentration in the ambient air moving onto the moorage (and the refinery) should also be determined so as to provide a background correction.

3.1.3 Carbon Tetrachloride/Perchloroethylene Manufacturing Plant

A. Background--

In the Task II volume, it was shown (Sec. 3.5.1.A) that carbon tetrachloride (CT) and perchloroethylene (perc) are produced by the same process. The yield is equimolar when methane is the starting material, but can be controlled to favor perc by substituting some or all of the methane with ethylene.

The only CT/perc manufacturing plant in California is at Pittsburg and is operated by Dow Chemical Company. The annual production of these chemicals is estimated at 20 and 22 million lbs/yr, respectively. The emissions are estimated to be 160 and 22 tpy, respectively, based on emission factors for each of the halocarbons published by different sources. As pointed out in the Task II volume, this large difference between the CT and perc atmospheric losses is highly questionable considering the nature of the process and the properties of the two chemicals. In any case, just this question and the magnitude of the CT emission rate underscore the need for testing at the Dow Pittsburg plant.

The person contacted at Dow was Mr. Bryant C. Fischback of their Research Center, Walnut Creek. Mr. Fischback participated on Task I of this program as a member of the panel of experts brought together by SAI to review the results of SAI's carcinogen selection and ranking process. When contacted, Mr. Fischback respectfully rejected the KVB request that the Dow Pittsburg plant be included in this test plan. The reason given was protection of process secrets beyond the capability furnished by any confidentiality agreement that might be employed.

B. Sampling Approach--

Because access to the Dow plant has not been extended, the only non-obligatory alternative available will be over-the-fence ambient air sampling. Emission factors would then be developed using virtual source modelling as illustrated in Appendix C of the Task II volume. While this approach is admittedly less accurate than conventional source testing procedures, it would settle the issue of the relative releases of CT and perc.

The Dow Pittsburg plant operates a wind monitor, the data obtained from which have been made available to the State (Ref. 59). For the ten years ending 1976, a clearly dominant pattern is seen in the wind data (see Table 3-5). For 63% of the time, winds are out of the southwest quadrant. The balance of the winds is about evenly distributed over the other three quadrants. In the southwest quadrant, the weight-averaged wind velocity is 8.7 mph. The best vector for sampling, radiating from the plant midpoint, would be 68° (true). The plant is located near the waterfront at Loveridge Road and 5th Street.

As can be seen from Figure 3-3, this wind vector penetrates New York Slough without intersecting the nearest public street, Waterfront Road. Even a due westerly wind (10% chance) barely provides a street curb sampling point. All of the property west of Waterfront Road is owned by Dow Chemical to some boundary to the weather side of the plant. This information was provided by the City of Pittsburg without specific cadastral research. Because of the wind conditions, sampling would have to be done from a boat. Winter Island, which is accessible by boat, could be used as a platform except for its distance. From the plant to the shore's edge is about 2,500 ft, and an additional 1,000 ft or so separates the island from Pittsburg on a bearing of 68°. Upwind sampling can be done on 5th Street.

SURFACE WINDS

TABLE 3-5. PERCENTAGE FREQUENCY OF WIND DIRECTION AND SPEED (FROM HOURLY OBSERVATIONS)

STATION:

STATION NAME: Pittsburg

YEARS: 1967 - 1976

MONTH: ALL

CLASS: ALL WEATHER

HOURS (L.S.T.): ALL

LOCATION: 38°01', 121°51', 10'

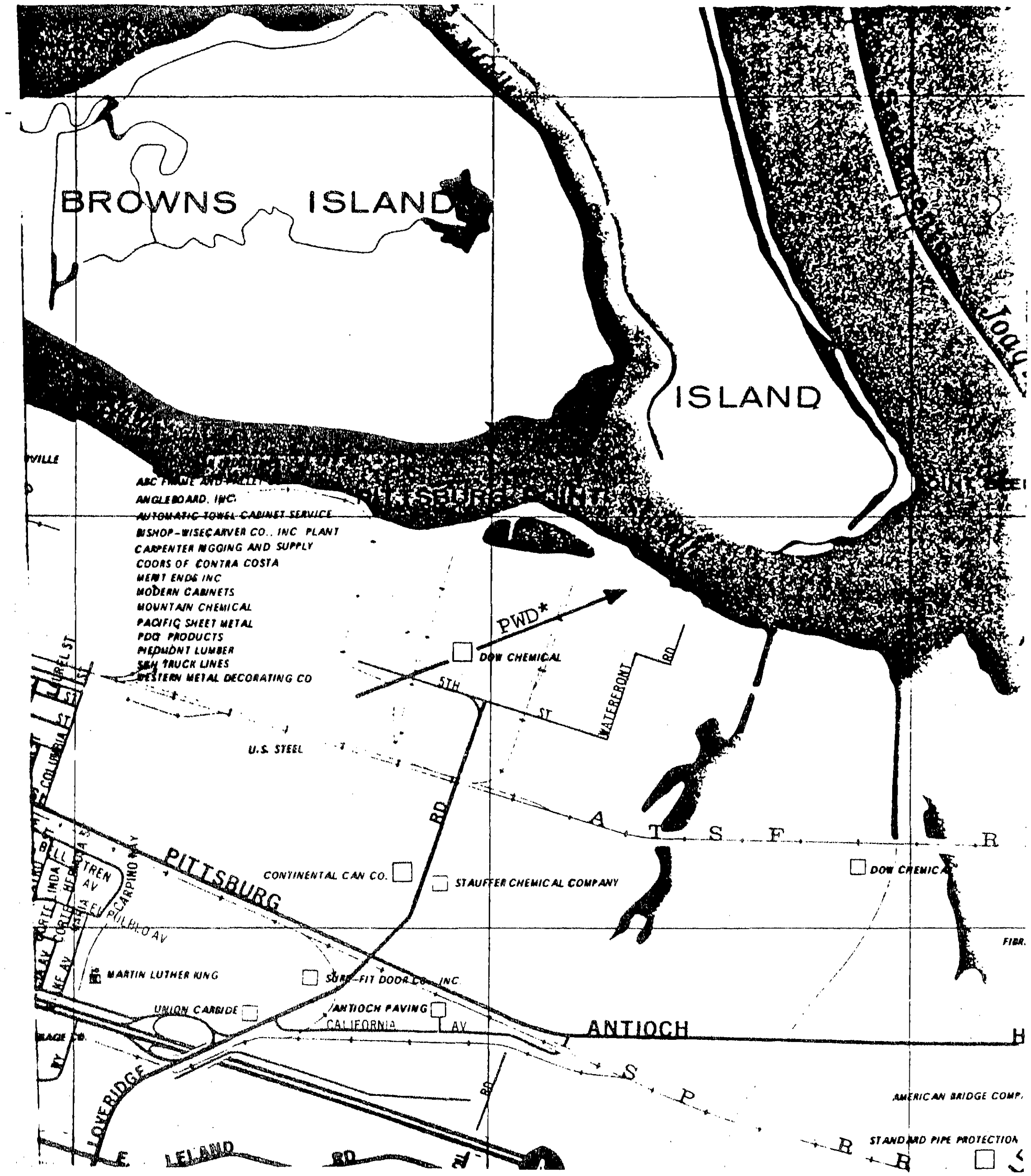
HEIGHT ABOVE GROUND: 25'

SPEED MPH DIR.	1 - 3	4 - 6	7 - 10	11 - 16	17 - 21	22 - 27	28 - 33	34 - 40	41 - 47	48 - 55	≥56	%	MEAN WIND SPEED
N												2	3
NNE												3	3
NE												5	3
ENE												5	4
E												4	4
ESE												3	4
SE												2	5
SSE												3	6
S												6	7
SSW												11	8
SW												16	10
WSW												20	9
W												10	8
WNW												5	6
NW												3	6
NNW												2	4
Calm	☒	☒	☒	☒	☒	☒	☒	☒	☒	☒	☒	100	7

DATA FROM DOW CHEMICAL CO.

TOTAL NUMBER OF OBSERVATIONS

Source: Ref. 59



* prevailing wind direction

Figure 3-3. Location of Dow Chemical Company CT/Perc Plant in Pittsburg

The sampling technique recommended for use is that developed by Pellizzari (Ref. 60). The highly dilute vapors of interest are concentrated on prepurified and prepurged Tenax GC (35/60 mesh) polymer bead adsorbent contained in 1.5 x 6 cm glass cartridges. Sampling rates of 1-2 ℓpm are used for collection periods of about one hour. If necessary, over 300 ℓ of air can be passed through channel-free Tenax collector tubes without fear of breakthrough of either CT or perc. Because the entire catch in each tube is then committed to a single analyses (see Sec. 2.3.1), parallel replicate tubes should be exposed when sampling. This can be done by using a manifold equipped with suitably sized critical orifices (checked before and after use) in each arm.

The use of this sampling equipment will be entirely practical while operating from a station consisting of a well-anchored boat. Meteorological instrumentation, which will also be required on board, will have to be lightweight and portable. The equipment used by Pellizzari in his many ambient surveys (including for CT and perc) should be suitable (Ref. 60).

He used a lensatic compass for following wind direction and for aligning the station with respect to the source. Wind velocity was measured with a Dwyer wind meter; a Biram-type anemometer would be preferred. Position relative to the plant can be accomplished using piloting (maneuvering board) technique, the accuracy of which will be enhanced by being at firm anchor.

Being near a deep-draft shipping channel, navigational charts showing prominent piloting reference points are available.

Air temperature (and humidity) can be recorded using a calibrated field-station apparatus equipped with a spring-wound recorder. Sigma meters will also be required to measure δ_w and δ_θ.

The test approach should conform with that outlined in Appendix A of Reference 50. At least 12 different stations should be sampled, with catches being taken over 4 one-hour periods during the early morning hours. Thus, three days of sampling will be required. Use of a tracer gas would be desirable if the plant management would permit a generator to be installed inside the plant.

C. Release Rate Calculation--

Reduction of data should involve the use of appropriately designed computer software (Ref. 50, App. A). After inputting measured parameters and assumed values (e.g., source height and center point) into the diffusion equation, source strengths will be calculated from the data obtained at each of the stations. After outliers have been discarded through variance analysis, the average release rate will be calculated. Since process rates will be unknown, the CT and perc release rates for the plant on the dates sampled will be the expressions output.

3.1.4 Carbon Tetrachloride Conversion Plant

A. Background--

The two major converters of carbon tetrachloride (CT) in California are Allied Chemical Company, El Segundo, and E.I. du Pont de Nemours & Company, Antioch. Both plants convert CT to trichlorofluoromethane and dichlorodifluoromethane which are called Freon (by du Pont) or Genetron (by Allied) 11 and 12, respectively, or simply F- or G- 11 and 12. Both manufacturers expressed willingness to cooperate in the development of the present test plan provided that process confidentiality was observed.

In Section 3.5.2B of the Task II Volume, unconfirmed estimates of CT consumed and ranges of CT emissions for the two plants were tabulated as follows:

ESTIMATED CT LOSSES FROM TWO FLUOROCARBON PLANTS

Plant	Annual CT Consumption, 10^6 lbs	Estimated Range of CT Emissions, lbs/yr
Du Pont, Antioch	50.2	20,000-502,000
Allied, El Segundo	17.5	10,000-265,000

The lower ends of the ranges comprise estimates offered by the operators while the upper ends are values derived using National Academy of Science factors. The span of these data in itself argues for the need of surveys to be performed to determine what the actual levels are.

Because both operators offered access to their plants, the Allied Chemical, El Segundo works was visited because of closer proximity to the project.

B. Site Visit--

On 5 September 1979, two KVB staff members were received by the Plant Manager, R. G. Cardinale and the Director - Technical Genetron/B & A Specialty Chemicals Division, Mr. R. E. Boberg. The latter gentleman happened to be visiting the plant at the time of the visit. Process details were not immediately released because a secrecy agreement had not yet been executed. The Plant Manager advised that all of the fugitive emission points in the system described had been leak-tested by a CARB team about a year earlier. This included valves, flanges, pump seals, and compressors.

The CT storage arrangement was inspected while a tank truck and trailer were being unloaded. A rail spur lay in the same area so that tank cars could be off-loaded through the same piping serving the tank truck. Piping, which was mostly of welded construction but with some threaded connectors, was traced to the brine-cooled storage tank and thence to the reactor. The tank breather, at the crown of the tank, was viewed. Capacities of the various units in this fairly simple arrangement were noted. During this tour, the only CT smelled or seen was about a gallon of liquid in a bucket that was used as a receiver for the priming leg of the transfer pump.

C. Sampling Approach--

The possible sources of emissions in a plant converting CT to fluorocarbons 11 and 12 are (1) the tails vent; (2) fugitive sources in the piping and pumping components; (3) the breather of the CT storage tank; and (4) transfer operations involving tank cars and trucks.

The Genetron tails tower serves as a process vent following the last distillation column. Because this stage is designed to condense the cryogenic G-12 (B Pt. -29 °C), the presence of significant levels of CT, which has a boiling point 106 °C higher, is not likely. A gas-flow measurement and grab sample of this vent will therefore suffice.

Leakage from valves, flanges, pump seals and related devices has been measured at the Allied El Segundo Works by a CARB team. A complete repetition of that work is therefore unnecessary. Data obtained in that survey, which was conducted over a year ago, should be used and a relatively few fittings rechecked. Because of their dynamic nature, all of the CT pump seals should be tested for leakage. A Davis Halide Meter will be suitable for this. If significant leaks are detected, the responsible components should be bagged and the leakage rates determined using a purge technique (Refs. 50 and 61).

The breather, a conservation-vent type, on the refrigerated CT storage tank should be tested. A bag should be taped around this device and gas outflow measured with a dry gas meter while the tank is being filled. A time-integrated sample should be taken using a lung-type Tedlar bag. Check valves should be provided to prevent reversing the test meter if flow direction changes. From the results obtained, CT loss can be related to fill rate and, thus, to plant process rate. With the same test apparatus CT losses during normal breathing can be measured. Because of the design of the storage tank, such losses will probably prove minimal.

A useful check will be to calculate the working and breathing losses of the CT storage tank using AP-42. Table 4.3.1 of the document furnishes physical properties for CT. The API breathing loss formula should, however, yield a higher emission value than would actually be measured. This is because the influence of diurnal temperature change as expressed in that formula would be diminished as a result of the tank walls being refrigerated.

CT loss during tank car or truck offloading will mainly arise from pump priming, accidental spillage, residual liquid in connector hoses and purging of the emptied tank. The last operation usually occurs at the plant filling the tanker rather than the receiving site.

The pump used to offload the tanker is primed by discharging some CT into a slop bucket set under the primer leg. If the practice is to leave this fluid to evaporate, the amount should be measured and listed as emitted. The number of primings (CT offloadings) occurring each each year should then be obtained from plant personnel.

Accidental spillage occasioned during several tanker hook-ups should be observed and estimates of liquid lost recorded. Average loss could then be multiplied by the same factor used for pump primings to estimate annual evaporation of spilled CT. Evaporation of CT left in the connector hoses can vary considerably depending on usage and hose-storage practice. A 1/8" deep puddle of CT in a 3 in. hose weighs 0.10 lb per running foot. Much of this residue can evaporate if the hose is plant property and is stored uncapped and exposed to sunlight. If conditions warrant it, special emission testing of the hoses should be considered.

D. Emission Factor Calculations--

The actual measurements recommended in the previous subsection should account for all possible CT emissions at the host plant. Thus, extrapolations to other process units will not be required. Since all of the emissions can be related to process rate, annual CT loss for the plant will be a straightforward calculation. Because Allied may not wish their CT production data to be released, the annual plant CT emission rate only may have to be reported.

Another factor that could impact the survey of the Allied Chemical Co. plant would be a shift-over from CT to chloroform as feed-stock. If this occurred, the test approach would still be essentially the same, however.

3.1.5 Ethylene Dichloride Production Plant

A. Background--

The only industrial facility in the State synthesizing EDC is that of the Stauffer Chemical Company at Carson. This plant manufactures the chemical primarily to convert it to vinyl chloride, the monomer widely used to produce polyvinylchloride (PVC). Because of the scrutiny that vinyl chloride monomer (VCM) plants have received since the halocarbon was found to have carcinogenic properties, Stauffer's Carson facility has been extensively tested for VCM but not EDC.

The process described in the Task II volume (Section 3.8, Figure 3-17) is basically that which is used at Stauffer. More precise information was furnished KVB by the company that includes obvious proprietary features. Stauffer required and KVB obliged in the execution of a secrecy agreement. Therefore, the present discussion will be based on the Task II process diagram cited, which is quite adequate for present purposes.

The production of EDC, as described in Section 3.8 of the Task II volume, involves a combination of two processes. In oxychlorination, ethylene gas is converted to EDC by contact with oxygen (in air) and hydrochloric acid. The latter is derived from the dehydrohalogenation of the produced EDC to form VCM. Because, however, the latter process yields only one mol of HCl for feed-back and EDC synthesis requires two, a make-up of the halogen source is needed. This is done by running a parallel direct chlorination process, i.e., adding chlorine to ethylene to form EDC. Theoretically, the stoichiometry would suggest that equal amounts of EDC would be produced by each process, oxychlorination and direct chlorination. The efficiency of the former and the holdback of any EDC from conversion to VCM (for solvent buyers) makes direct chlorination the dominating process.

When the Task II volume was prepared, Stauffer reported substantial sales of EDC out of Carson. When visited, the plant was importing EDC and trans-shipping only about a tank-truck per month of the halocarbon. This is consistent with the Task II findings, since of the two of the few EDC solvent users estimated to be operating in the State, both indicated incipient or ongoing activities which would eventuate in the phase-out of EDC.

Stauffer management was quite cooperative and provided process diagrams, plant lay-out drawings and a narrative description of ongoing production status and APC equipment installation plans. Correspondence from their home office, Westport, Conn., corrected, in some detail, parts of the Task II text pertaining to Stauffer, and dismissed, as grossly inaccurate, the release estimated for EDC that is given there (0.3 to 3.2 x 10^3 lbs/yr). KVB is inclined to agree that the high end of that range is improbable.

B. Plant Visit--

The Stauffer plant was visited on 15 October 1979. It was noted that all process vents for both VCM and EDC vessels were ducted off to two waste heat boilers equipped with natural gas burners. Because the emission levels of VCM from the stacks of these boilers have been found to be acceptable, it is unlikely that EDC levels would be significant.

The fixed-roof tankage used at the Stauffer plant for EDC storage is all vented to the atmosphere. Some of the tank vents are equipped with driers but these are nonfunctional. Stauffer plans, however, to duct all EDC tank vents into the piping system connected to the two gas incinerators mentioned above. This would effectively limit EDC releases to fugitive effects at valves, flanges, and pumps plus any losses occasioned by the now infrequent transfer of EDC to tank trucks.

C. Sampling Approach--

The <u>current</u> release paths for EDC emissions at the Stauffer plant have been identified as the following:

- Pump and piping fixture leakage
- Storage tank vents
- Gas incinerator effluents
- Loading of outbound tankers

As suggested in the preceding text, the last two operations probably involve minor releases but perhaps should be verified. In the case of the waste heat boilers, grab sampling and compositional analyses would be adequate for being incorporated in the present test plan. Atmospheric losses of EDC during the loading of tank trucks can be estimated from related emission factors published for a number of solvent products. The key input for this computation will be traffic data for the Stauffer plant.

These two (probably) minor sources aside, primary interest will be on (1) fugitive sources comprised of valves, flanges and pumps; and (2) the EDC tank vents. The latter would not be considered, however, if the plan contemplated by Stauffer for bringing the tank breathers into the vent gas incineration system were soon to be implemented. In any case, actual sampling of the tanks would be unnecessary since the characteristics and composition of the contents are reasonably fixed and well known. Working and breathing losses can be calculated from AP-42 data, Table 4.3-1, which furnishes physical property data for EDC under its I.U.C. designation, 1,2 - dichloroethane.

For the detection and sizing of process leaks from valves, flanges, and pumps at the Stauffer plant, the approach recommended for the Chevron refinery (see Section 3.1.2) will not be appropriate. This is because the Radian nomographs correlating TLV Sniffer readouts with hydrocarbon mass release rates would not be applicable to halocarbons. According to Bacharach Instrument Co., the manufacturer of the instrument, EDC furnishes a response that is 23.8% that of an equivalent amount of hexane. This sensitivity difference is by no means preclusive, but the conversion of Radian hydrocarbon data to an EDC nomograph using that factor would be risky. An element in this would be the presence of ethylene in any of the process streams which would then bias upward any indicated EDC leaks.

In view of these considerations, the survey technique used in the ARB hydrocarbon emissions study (Ref.50) is recommended. A large fraction of the fittings population included in the EDC synthesis storage and conversion process piping would be soap tested. Leakers would then be tagged and selected low, medium and high leak-rates flow-calibrated by bagging these components and measuring mass flows. This can be done by either having the leak itself drive the train or by purging the bag and analyzing the purged effluent for its content of leaked vapor. The leak rates from all the tagged components can then be estimated from this coarse calibration. Where neat streams of EDC are involved, the mass rate can be calculated directly. Where process streams of mixed components are involved, it will be necessary to bag representative leakers in each of such streams and acquire samples for compositional (GC) analyses. This will not be necessary in runs that have no leaking valves or flanges or where the contents of the lines have been compositionally well established by the Stauffer analytical laboratory. Acquisition of fugitive emissions for compositional analyses can be done in Tedlar bags, provided the contents are quickly committed to GC determination. The presence of ethylene would tend to rule out the use of polymeric or charcoal adsorbents because of its poor retention on such media. Most of the streams, however, contain little if any ethylene, in which cases Tenax or charcoal may be considered. Once the typical mol-fraction of EDC in such streams has been determined, then the mass flow rates from the identified leaking valves and flanges can be calculated.

The testing of pumps (no compressors were seen, but these may also exist and require testing) will involve both aqueous and organic streams. The former streams may contain EDC, which is appreciably soluble (0.9 wt/wt % @ 20°C). Because the number of pumps moving EDC containing liquids is not great, all such active pumps can probably be tested. A leak survey should first be performed using the TLV Sniffer or Century OVA system (photoionization leak detection instruments are "blind" to EDC). Pumps found to have leaky seals can then be bagged and the fugitive emissions measured in the same manner as valves or flanges.

Another possible source of EDC release is the process water that has contacted that chemical and then has been stripped of it. Samples of this wastewater from such operations should be checked for residual EDC using the Bellar and Lichtenberg technique (Ref. 57). If the levels warrant, air sampling over the associated process drains may be appropriate. Similarly, cooling tower feedwater may also contain EDC and should be checked by the same lab method. If any EDC is found to be present, evaporating EDC release can then be determined by comparing its level in the effluent and influent after correcting for any flow differences in the two streams (i.e., makeup + blowdown + windage + drift + evaporative loss).

3.1.6 Secondary Lead Smelter

A. Background--

As pointed out in the Task II volume (Sec. 3.1.2.C(2)), almost 30 tpy arsenic are estimated to be emitted by the four large secondary lead smelters operating in California.

The lead production and arsenic emissions estimated for these four plants are as follows:

SECONDARY LEAD SMELTERS IN CALIFORNIA

Company	Location	Estimated Annual Lead Production, 10^3 tons	Estimated Annual Arsenic Emissions, lbs
Gould, Inc.	Vernon	50	44,000
RSR Corp.	Industry	7.5	6,600
Southwest Smelting	San Bernardino	5	4,400
ARCO-Pacific	Carson	5	4,400
	TOTALS	67.5	59,400

Because of cost constraints, the planning strategy is to test only one mill and preferably the largest (Gould, Inc). Expecting refusals of cooperation, three of the four were contacted, Southwest Smelting being omitted because of its distance.

Following preliminary telecon explorations, letters were requested by each person contacted and these were sent in confirmation. Gould replied and granted permission for source testing provided that the sampling teams had proper insurance coverage and did not interfere with plant operations. Process information would be made available by Gould but would have to be treated as being proprietary. A preliminary site visit was permitted by Gould and accordingly arranged.

B. Site Visit--

On 10 August 1979, the secondary lead smelter operated by Gould Inc., Metals Division, was visited. This plant is located at 2700 So. Indiana St., Vernon. The plant appeared to be in normal operation with no unusual maintenance activities in progress. There were no visible dust emissions from any of the stacks standing in the complex.

The Plant Industrial Hygienist, Mr. J. E. Dionne, served as guide while the Plant Engineer, Mr. Ali Ghawami, provided process data. The latter included all of the inputs specified on the KVB Test Preparation and Plant Visit form and a complete plant layout drawing. In correspondence with Messrs. Dionne and K. G. Ford (Gould staff engineer, Mendota Heights, MN), it was stipulated that these data would be treated as proprietary.

The present discussion accordingly avoids the release of specific process information. The plant does, however, operate all of the major types of secondary lead smelter furnaces. These include the reverberatory furnace, the blast furnace or cupola and pot furnaces (for remelting, alloying and refining by drossing). A bulk of the output is produced by continuous process so that conformance with a batch melt duration is not required during testing.

All of the thermal processes operated in the plant are vented into air suction systems that are ducted to bag houses. It is possible, however, that fugitive emissions are released since air management is not entirely an enclosed process, particularly around the remelting, alloying and refining pots.

On the ducts leading to the stacks, sampling ports are located at accessible but crowded points two to four feet above cat-walk platforms. All of the ports are at least 20 ft from any duct bend or other point of disturbance. All of the test holes are from 2 to 2.5 inch diameter.

According to AP-40, the highest arsenic emissions can be expected from the blast furnaces. These produce hard or antimonial lead that may contain up to 0.5% arsenic. The reverberatory furnace discharges about half the dust that the blast furnace does and the product is semisoft (a purer) lead that contains considerably less arsenic than antimonial lead. The pot furnaces produce soft lead that is typically 99.9% even when alloyed with other metals (including arsenic). The pot furnaces used in remelting, refining (by drossing) or alloying are relatively quiet and would be expected to release the least amount of arsenic.

C. Sampling Approach--

Because the efficiency of the air cleaning equipment is in conformance with regulations, there will be no point in verifying this. Therefore, it is recommended that only the cleaned effluent be tested. By sampling the cleaned gas from the reverberatory furnace, one blast furnace battery, and one or two groups of pot furnaces, an emission factor for the entire plant should be calculable.

An EPA reference method for determination of particulate and gaseous arsenic emissions from non-ferrous smelters is shortly to be released. The sampling technique is basically the same as the standard EPA Method 5 technique except that six impingers instead of four are used. The first two contain water, which retains any gaseous arsenic passing through the filter. The last three impingers, containing 10% hydrogen peroxide, are included for the purpose of retaining sulfur dioxide. If this analyte is not of interest, then the standard four-impinger train will be satisfactory. The third impinger (in either arrangement) will contain indicating silica gel. The rinse liquid for the probe filter holder and emptied impinger tubes is N/10 sodium hydroxide.

Thus, employing the Method 5 approach, the largest duct that would have to be sampled leads from the reverberatory furnace bag house to a brick stack. Because the nearest upstream bend is over 8 duct diameters away, the minimum number of traverse points would be 12, according to EPA Method 1. No less than 8 traverse points are indicated for any of the ducts.

On completion of the tests, the filters, impinger liquids and rinsing will be taken to the laboratory for arsenic determination as described later in Section 3.1.3.

D. Emission Factor Calculation--

Based on the process rates of the furnaces sampled, arsenic emission factors will be calculated. The unsampled other furnaces of the same types will then be assumed to release the same amounts of arsenic per unit of throughput. Then, from the annual production for all furnaces of each type, the plant temporal emission factor can be calculated. The annual lead production for all furnaces will be considerably higher than the plant's lead sales, since large fractions of the reverberatory and blast furnace production is remelted for purification and alloying.

Because Gould will probably not wish lead production data to be released, the annual plant arsenic emission only may have to be reported without reference to output.

3.1.7 Asbestos Mining & Milling Operations

A. Background--

In the Task II study (Section 3.2), it was estimated that the three mining and milling operations in California accounted for over 90% of the 230 tons of dust released by all facilities processing asbestos. It was strongly noted, however, that the fractional amount of asbestos in these dust measurements was uncertain. This conclusion was based on the fact that specific asbestos determinations had not been attempted or inadequate asbestos measuring techniques (see Section 2.2 of this volume) were used in many of the cases.

Of the three mining/milling operations, the Calaveras Asbestos Company facility at Copperopolis scaled highest using an arbitrary hazard formula. This is shown in Table 2-1 of the Task II volume. The other two facilities are operated by the Atlas Asbestos Company 32 miles north of Coalinga and the Union Carbide Company near King City. Neither appeared on Table 2-1 because of low scaling factors. In the case of the Atlas mine, no urban populations exist within the 100 sq km square in which the mine is centered. The Union Carbide Company mine scaled at a low value because the EIS-estimated dust emissions for that facility (3 tpy) are considerably lower than for the other two mines (Atlas: 56 tpy; Calaveras: 146 tpy).

In the case of the Calaveras mine, which lies about 3 miles east (103° true) of Copperopolis, population density is quite low. The town of Copperopolis has a population of only about 350 people while perhaps another 150 people are accounted for at the nearby New Melones Dam, and settlements on the shores of Tulloch Reservoir.

A large fraction of the estimated dust emissions from the Copperopolis mine is associated with fugitive effects occurring out-of-doors. Some 85% of the EIS dust emissions are associated with pit blasting. According to a mine official, pit blasting is not done when the winds are up and on either Copperopolis to the west or the New Melones damsite to the east. The accurate measurement of open pit dust emissions is of course unachievable.

Because of the otherwise remote nature of the Copperopolis mine, it is probable that pollution of the ambient air will have its principal impact on the few nearby villages. Given easterly winds, asbestos levels in Copperopolis would be of greatest concern, while on an arc 6 miles from the mine would be the smaller settlements of Melones, Carson, and Frog Town on winds from the southwest to the south southwest, respectively. Depending on prevailing winds, the measurement of asbestos at these points would be more meaningful in terms of nonoccupational health impact than attempting to derive an overall emission factor for the mine itself.

The wind patterns in the area have not been well characterized. No data had been acquired near here by the California Department of Water Resources, the Energy Commission or the Forestry Service. Limited data (summer only and for two morning hours) had been taken by the last State agency near San Andreas and at Sutter's Hill, both of which stations are too far from the mine to be of much value. Mr. Wm. Innes, Meteorologist in the Forestry Service, predicted that marked diurnal changes would likely operate in the Copperopolis/New Melones Dam zone. The pattern would probably feature westerly and southwesterly winds during the day followed by nighttime flows out of the northeast to east.

Other weather sources consulted included the Environmental Impact Statement (Ref. 62) filed by the Army Corps of Engineers in May, 1972, for the New Melones Dam project. No wind data were provided. Wind velocity maps (Ref. 63) published by the Geological Survey indicated that the area may have annual mean wind velocities of less than 11 mph.

B. Sampling Approach--

A two phased approach is recommended wherein characterization of asbestos fall-out in inhabited areas near the mine would eventuate. The first step would involve the characterization of the wind patterns in the area. Although arrangements were not formalized, it is believed that the Calaveras Asbestos Company will allow the meteorological gear to be set up on their property. This view is based on a conversation held with a mine executive who serves as Environmental Specialist.

Wind direction patterns and velocity should be continuously recorded over enough periods of the year that dominating trends can be identified. Using assumed diurnal source strengths and particle size distributions, diffusion modeling should then be undertaken to determine the rough level of dust delivery to the various inhabited areas near the mine. From this analysis, the village(s) likely experiencing the greatest emissions from the mine will be recognized. Although the ambient asbestos values calculated in this modeling may be very inaccurate, only the relative rates of transport of asbestos to the receptor sites is of interest.

The second phase of the work will be to determine ambient asbestos levels at the village(s) found to be most susceptible to asbestos pollution. This should be done using polycarbonate membrane filters (0.4μm)* on hi-vol samplers at appropriate sites in the village(s). Two to three 24-hour runs at each of the stations should be made. The collections should be acquired only when normal operations are ongoing at the mine and when the previously determined weather conditions prevail. Meteorological measurements should be made while sampling is being done.

Sample analysis should include TSP measurement in addition to TEM determination of the asbestos fraction (see Section 2.1.3). Establishing the asbestos content of the ambient airborne dust will be a useful determination in its own right.

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* Studies have not been conducted to determine if finer pore size would result in higher asbestos retention.

3.1.8 Power Plants

A. Background--

In Section 3.1.2.D of the Task II volume, it is stated that an estimated 17,600 lbs/yr of arsenic are released by oil-burning power plants. This estimate is not well supported and should be verified.

Assuming a distribution of this release in proportion to power production, three power plants ranked with the seventeen "hot spots" tabulated in the Task II hazard scaling shown in Table 2-1 of that volume. These three plants were among the six lowest ranked on that list. The three were each estimated to release between 1600 and 2000 lb/yr arsenic. The three plants are at Pittsburg (PG&E), Long Beach (SCE), and Salinas (PG&E).

The KVB staff is quite familiar with all types of boiler operations and configurations. Because of this and the fact that KVB is almost continuously in the service of the electrical utility conpanies, no formal effort was made to contact any utility regarding the present planning. Unlike many of the other facilities discussed here, the testing of a power plant is relatively simple. In fact, the filter catch acquired during a routine TSP measurement would probably adequately serve the needs of the present survey.

Because testing will be done on a single unit basis, there will be no point in testing a power plant that is one of the top power producers in the State. The unit tested should, however, be of a popular size. The unit sizes of the three power plants cited above lie within the following ranges:

UNIT SIZES OF CALIFORNIA'S
THREE LARGEST POWER PLANTS

Plant	Operator	No. of Steam Units	Capacity Range of Steam Units, MW
Moss Landing, Salinas	PG&E	7	115-739
Contra Costa, Pittsburg	PG&E	7	115-340
Los Alamitos, Long Beach	SCE	6	175-480

B. Sampling Approach--

Standard EPA Method 5 traverse isokinetic sampling should be used. Penetration at the standard sampling ports will be quite acceptable. It is possible that at typical flue gas temperatures (∿ 150°C) some volatile arsenic may exist. Arsenic trioxide, which is more volatile than the metal, has a boiling point of 457°C. This is low enough to suggest that the vapor pressure at 150°C may be significant in terms of sampling requirements.

Any arsenic vapor flowing through the filter would then pass through the first two (wet) impingers. This has been addressed in the new EPA arsenic reference method that will soon be released. (See Sec. 3.1.6C.) The only essential difference is that arsenic is determined in the scrubber liquid (water) as well as the filter and the system rinse liquid is N/10 NaOH. Additional impingers are also provided for SOx determination but that is not of concern here.

3.1.9 Asbestos Consuming Plants

A. Background--

In the Task II survey, it was estimated that about 700 plants in the State are involved in the manufacture of asbestos-containing products, involving release of some 23 tpy of asbestos fibers. These asbestos consumers range widely in the character of their manufacturing processes but can generally be classified as operations in which fiber-containing dusts are ducted away from the working environment and are vented into the atmosphere with or without APC equipment intervening. Many of these processes have been monitored for TSP emissions but few have been surveyed specifically for fibrous asbestos releases. Where the latter has been done, questions often exist concerning the reliability of the counting procedures used (see Section 2.2 of this volume).

Unlike the three asbestos mines operating in the State (see Section 3.1.7 of this volume), most of the asbestos consuming industries are located in urban areas of high population densities. In terms of EIS emission factors, few such plants have been listed as having dust release rates of over 1 tpy. This level of control doubtless reflects the influence of the National Emission Standards for Hazardous Air Pollutants (NESHAP), which allows no visible asbestos emissions.

Based on the EIS print-out, the asbestos consuming plant listed as emitting the largest (19 tpy) amount of dust is the Johns-Mansville asbestos cement pipe factory in Stockton. Since the product is about 15% asbestos, the released dust could have the same composition. This is doubtful, however, since bag houses are used at the J-M Stockton plant, which is located at Sperry Road and Airport Way. These APC devices should preferentially show greater efficiency for the fibrous asbestos moiety than for the more spherical cement particulates.

The amount of asbestos in the dust emitted by the J-M Stockton plant has not been determined by the San Joaquin County APCD. Johns-Manville itself did conduct such measurements over a four-year period on the six bag house vents it identified as being the only possible release points. The results, which are shown in Table 3-6, are all based on optical microscopic measurements. As pointed out in Section 2.2 of this volume, that technique yields counts badly biased to the low side. Table 3-6 does, however, furnish useful vent data that can be presented here without violation of the usual proprietary restrictions encountered on this study.

Negotiations with J-M were through the Manager of Community Environmental Control, Mr. J. N. Siegfried, in Denver, CO. A visit to the Stockton plant was requested but could not be arranged in the several months ensuing. Mr. Siegfried did not, however, specifically deny the request. Rather, he suggested that a site visit would be needless since the data he furnished (Table 3-6) satisfied any testing requirement that the project might require. It was pointed out to him that the optical microscopic technique used to generate the data was inherently inadequate and yielded low values (see Sec. 2.2). It is assumed that future plant access for the purpose of acquiring more acceptable data may be forthcoming.

According to the San Joaquin County APCD (SJCAPCD), the J-M Stockton plant operates under two permits. One is for asbestos cement handling operations and the other for scrap recycling. The plant produces a rated 15,000 tpy of asbestos cement pipe per year.

Table 3-6

ANALYSIS OF ASBESTOS FIBER EMISSIONS

REPORTED BY JOHNS-MANVILLE FOR THEIR STOCKTON PLANT

Control Apparatus Exhaust Sampled	D-1	D-2	D-3	D-4	D-5	D-6
No. of separate tests involved	4	6	4	3	5	5
Avg. optical count; fibers/cc	3.7	1.1	0.2	0.5	0.5	0.4
Exhaust air flow; ACFM	18,000	26,000	8,000	13,000	53,000	32,000
Typical annual operating hrs ($x10^3$)	6.0	6.0	3.2	3.2	6.0	6.0
Annual emission; fibers/year ($x10^{13}$)	67.89	29.15	0.87	3.53	27.01	13.05
Calculated annual mass emissions (lb)	18.1	7.8	0.24	0.95	7.2	3.5

Total plant annual mass emissions of asbestos fiber = 37.7 lbs

Analytical notes: Samples for fiber counting retrieved from membrane filters which were employed to intercept airborne fibers on the clean-air side of the baghouse collection units during normal service. Technicians responsible for laboratory analysis work estimate that the average fiber counted had a diameter of about one micron (0.9 to 1.1) and an approximate length of six microns (4.0 to 8.0). Conversion of fiber counts to mass are based upon these estimates and a density for chrysotile asbestos fiber of 2.56 grams per cubic centimeter. The weight of an average single fiber therefore is calculated to be 1.206 x 10^{-11} grams.

Production involves the processing of asbestos through a willowizer and mixing with sand, cement and water to produce a slurry. This is sheeted and rolled on to steel mandrels to furnish the desired pipe diameters and dried. The shapes are then kiln dried for 10 hours with 300°F steam to produce the finished product. This portion of the operation and particularly the initial mixing step is extensively ducted to minimize health hazard, the air flows from which are handled by four bag houses (D-1, D-2, D-3, and D-4 of Table 3-6).

Waste, in the form of broken pipe and bag house dust, is recycled, the former being first reduced in ball mills. Suction air removed from the dump and storage area for this area and the ball mills is led out to bag houses. Table 3- 6 lists two (D-5 and D-6) while the SJCAPCO lists three (an ICA, a Mikropul and a Reese) bag houses for handling dust from scrap recycling. This discrepancy will have to be clarified.

The SJCAPCD rates the bag houses as 98% efficient and assigned dust input at 127.5 lbs per ton of pipe output. Thus the plant dust emission factor of 19.12 tpy obtains (annual pipe production being as stated earlier, 15,000 tpy).

Other emission sources are refuse piles situated in the north yard of the plant. Broken or rejected pipe too large to feed into the ball mill is piled and crushed by a bulldozer. This occurs about twice a year and, although the pile is wetted down, the all-day operation does occasion dust releases. Another pile was maintained where bag house dust was discarded. This very fine material was sprayed with a sprinkling system to prevent mobilization. An EPA inspection in March of 1976 resulted in a report critical of this practice (all of the pile was not wet). The SJCAPCD subsequently noted that bag house dust was being added to the recycled scrap material but recommended that this be verified as current practice.

B. Sampling Approach--

Sampling of the 6 or 7 bag house effluent vents should be done by the EPA Method 5 technique. Polycarbonate membrane filters (0.4μm pore size) should be used so as to conform with the substrate requirements of the provisional EPA transmission electron microscopic technique (see Section 2.1.3 and Ref. 26). It is assumed that plant access will be permitted and that process rates will be made available.

An analysis of the air duct system should be made to determine if any of the bag houses are receiving compositionally similar dust streams from like process elements. If such flow arrangements are noted, it may be possible to reduce the number of bag house vents that are sampled and, instead, extrapolate the asbestos catch from one to the other, using flow ratios.

Although the existence of significant fugitive dust emissions from within the plant appears unlikely, the situation in the north yard is unclear. This area should be inspected to determine if the bag house dust pile has been removed (for recycle) or, if still intact, is adequately protected against wind erosion. Other sites for dust mobilization exist along the roadways and in ditches. These should also be evaluated and hazardous conditions noted.

C. Emission Factor Calculations--

It is assumed that process rates will be made available and that emission factors for each bag house can be calculated on the basis of pipe output during the period of the testing. Because the scrap recycle operations will yield dust in proportion to the level of these activities and not necessarily pipe production rate, it will be important that sampling be done when both rates are normal with respect to each other.

In computing the annual asbestos emission factor, it will be well to include TSP as well. This will require that the catches be gravimetrically determined as well as being counted by TEM for asbestos.

3.2 SPECIAL TESTING

Emphasis on the present program has focused on stationary sources or "hot spots" that may affect surrounding local populations. Discussions were offered on area and dispersed sources which, in some cases, were estimated to be considerably larger in total than all combined stationary sources emitting the same pollutant. Although it was not within the scope of the present program to consider test planning for such sources, an itemization of these problems is considered worthwhile. This has been done in Table 3-7. This tabulation provides a reference to the pertinent Task II discussion on the problem, dimensions the estimated release rate and receptor area, and suggests the type of testing that appears warranted. The pollutants of interest are again alphabetically listed.

TABLE 3-7. SPECIAL TESTING OF NONSTATIONARY SOURCES SUGGESTED BY PROGRAM FINDINGS

Pollutant	Source	Task II Vol. Page (s)	Estimate Emissions, tpy	Receptors	Testing Recommended
Asbestos	(1) Demolition of Buildings	3-32	Unknown	(a) Demolition Workers	(a) Personal Samplers
				(b) N.P.*	(b) Virtual Source Method
	(2) Erosion of Serpentine Deposits	3-32	Unknown	(a) Recreationists	(a) Personal Samplers
				(b) N.P.	(b) Hi-Vol Sampling of Fall-Out
Benzene	(1) Gasoline Distribution & Marketing	3-56	1100	G.P.†	None: Adequate Testing Already Done
	(2) Automobiles	3-58	26,000	G.P.	Exhaust & Sweat Box Testing
Cadmium	Automobiles	3-67	7	G.P.	Roadside Hi-Vol Sampling
Ethylene dibromide	Fumigated Fields	3-94	<250	(a) Farm Workers (b) N. P.	(a) Personal Samplers (b) Ambient Air Sampling
Nitrosamines	Almond Orchards Sprayed with Ziram, Thiram or Ferbam	3-13	Unknown (Possibly Unknown)	Farm Workers	Personal Samplers

*N.P = Neighboring Populations
†G.P.=General Population

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APPENDIX A

BATTELLE COLUMBUS LABORATORIES METHOD FOR PAH ANALYSIS

APPENDIX A

ANALYSIS OF PAH

The PAH analytical procedures used at Battelle consist of sample extraction and concentration, liquid chromatographic cleanup, and analysis and quantitation in a glass capillary gas chromatograph (GC) with flame ionization detection or GC/MS.

Extractions are carried out using only "Distilled in Glass" solvents to avoid contamination of the sample with the significant amounts of impurities found in other grade solvents. Samples obtained by adsorption onto a porous polymer adsorbent (such as Tenax or XAD-2) are Soxhlet extracted with an appropriate solvent for 24 hours. Pentane is used for Tenax extractions, while the solvent of choice for XAD-2 is methylene chloride. Filters are extracted with methylene chloride by ultrasonic agitation for 1 hour. Water samples are extracted with methylene chloride (10% of water volume), separated, and methylene chloride is dried over magnesium sulfate.

At this point, all samples are spiked with a standard solution of 9-methylanthracene, 9-phenylanthracene and 9, 10-diphenylanthracene at a level of 5 μg per compound. The samples are reduced to a volume of about 10 ml by use of a Rotovap. Samples in methylene chloride must be solvent exchanged into cyclopentane to insure proper LC separation. Thus, at this point, 15 ml of cyclopentane is added to the sample and the volume reduced to 0.5 ml by Kuderna-Danish evaporation.

The sample is then liquid chromatographed on silica gel to remove interfering species. The column is slurry packed (methylene chloride) with 10 g of 100-200 mesh silica gel and washed with 40 ml of petroleum ether. A 25 ml fraction of petroleum ether and a 20 ml fraction of 20% methylene chloride in petroleum ether are collected and discarded. The PAH is eluted with 75 ml of 20% methylene chloride in petroleum ether. The fraction is then reduced to a convenient volume (usually about 1 ml) by use of a Kuderna-Danish concentrator.

The analytical scheme involves a glass capillary GC/MS procedure which separates many of the PAH isomers (including BaP and BeP) with only one chromatographic run. A 30 m SE-54 (or other similar column) capillary column is directly coupled to the mass spectrometer via a glass-lined transfer line. The gas chromatograph is equipped with a Grob-type injector enabling both direct and split (for very concentrated samples) injections. The column is temperature programmed from 160 - 250 C at 2 C/min. Injector and transfer line temperatures are at 280 C.

Sensitivity is improved by the use of single ion monitoring. We simultaneously monitor the molecular ions of up to eight compounds of interest. Quantitation is achieved by ratioing the ion current of the molecular ion of interest to that of the internal standard and applying a calibration factor to minimize the differences in ionization efficiencies of the compound and the internal standard. The use of single ion monitoring minimizes interferences from fragmentation of extraneous compounds which may not have been removed during the liquid chromatographic cleanup.

A four point standard curve is determined for each of the five PAH's using three internal standards. The ion currents of anthracene and pyrene are ratioed to that of 9-methylanthracene; chrysene is ratioed to-9 phenyl-anthracene; and perylene and indeno (1,2,3-cd) pyrene are ratioed to 9,10-diphenylanthracene. The computer determines a calibration factor for each of the 5 PAH's which minimizes the differences in ionization efficiencies between the PNA and its internal standard. The computer performs a least square analysis and provides a correlation co-efficient and intercept (the detection limit). The correlation coefficient is a least 0.990 for an acceptable calibration curve.

By assuming that similar PAH's have similar ionization efficiencies, calibration curves are generated using the previously determined calibration factors. For example, methylanthracene uses anthracene's calibration factor; fluoranthene, and methyl pyrenes/fluoranthenes use pyrene's factor. Benzo(c)phenanthrene, benz(a)anthracene, dimethylbenz(a)anthracene, and the methylated chrysenes are referenced to chrysene. The benzfluoranthenes, benzo(a)pyrene,benzo(e)pyrene, and methylbenzpyrenes are referenced to perylene. Methylcholanthrene,benzo(ghi)perylene,dibenz(a,h)anthracene, dibenzo(ai,ah)pyrenes and coronene all use the calibration factor determined for indeno(1,2,3-cd)pyrene.

Sample quantitation is achieved by ratioing the ion current of the molecular ion of interest to that of the proper internal standard and applying the previously determined calibration factor.

The GC/MS system used for PAH analysis at Battelle, consists of a Finnigan Model 9500 biomedical-type gas chromatograph coupled with a Finnigan Model 3200 mass spectrometer. Data collection and processing are handled by a System Industry Model 250 data system which utilizes a DEC (Digital Equipment Corporation) 16K PDP 8 m computer.

The glass capillary system used has excellent separation efficiency. It is capable of obtaining baseline separation of benzo(a)pyrene from benzo-(e)pyrene, benz(a)anthracene from chrysene, and phenanthrene from anthracene. Furthermore, partial separation is achieved for benzo(b)fluoranthene from benzo(j and k)fluoranthene.

The detection limit for each PAH compound is about 0.1 μg per total sample. The precision of the method varies for the different compounds, but is in all cases better than 25 percent.

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