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Sampling and Analysis of Trace-Organic Constituents in Ambient and Workplace Air at Coal-Conversion Facilities

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MASTER

ARGONNE NATIONAL LABORATORY
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July 1980

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SAMPLING AND ANALYSIS OF TRACE-ORGANIC CONSTITUENTS IN AMBIENT AND WORKPLACE AIR AT COAL-CONVERSION FACILITIES

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ABSTRACT

A review of the recent literature reveals that current sampling procedures involve the use of glass fiber filters for particulate-sorbed organics and sorbent resins such as Tenax GC and XAD-2 for vapor-phase organics. Ultra trace-organic analysis of air pollutants or particulates may require the collection of a large (1000-3000 m³) sample by a high volume air sampler. Personal air sampling requires a smaller sample (≈ 0.5 m³) and a portable collection apparatus.

Trapped organic chemicals are recovered by solvent extraction or thermal desorption of the collector. Recovered organics are separated by using liquid chromatography or gas chromatography and are identified by ultraviolet or fluorescence spectroscopy, gas chromatography, or mass spectrometry. For quantification, standards are added to the air stream during sampling or to the filter or resin following sampling.

Analysis of the requirement for air sampling in and around coal conversion plants, coupled with the findings of the literature review, indicates that a combined particulate-filter and solvent-extractable-resin sampling unit should be used to collect both particulate-sorbed organics and vapor-phase organics from workplace or ambient plant air. Such a sampler was developed for stationary, moderate-to-high-volume air sampling. Descriptions of the sampler are provided together with sampling efficiency information and recommendations for a sampling procedure.

1 INTRODUCTION

1.1 BACKGROUND

The existence of huge reserves of coal in the United States, coupled with the adverse economic effects of both potential natural gas shortages and the trade imbalance caused by the importation of large quantities of oil, has caused renewed interest in coal conversion technology. Coal conversion produces high-Btu, pipeline-quality gas to replace dwindling supplies of natural gas as well as coal liquids to replace increasingly expensive imported crude oil. In a recent Oak Ridge National Laboratory (ORNL) review of the environmental, health, and control aspects of coal conversion, coke oven

workers were shown to experience a higher risk of developing cancer than the general population (ORNL, 1977).

In order to evaluate worker exposure to hazardous emissions from commercial gasifiers, it will be necessary to identify emissions in the workplace air of pilot plant gasifiers that are now being tested. Because the chemical composition of coal is complex and varies from one coal seam to another, fugitive gaseous emissions from a coal-gasification plant also can be expected to be complex and to contribute a wide array of organic compounds and volatile trace elements to the surrounding air. In addition to carbon and hydrogen, coal contains nitrogen, sulfur, oxygen and trace elements. Based upon the analysis of coke-oven emissions, aliphatic hydrocarbons, aromatic hydrocarbons, polynuclear aromatic hydrocarbons, nitrogen and sulfur heterocycles, acids, alcohols, and phenols may be found in plant emissions as well (Lebowitz et al., 1975).

Typical urban air contains numerous organic compounds that originate from the burning of fossil fuels. A significant source is the internal combustion engine (Grob & Grob, 1971; Perry and Twibell, 1973). Michael Guerin of ORNL (personal communication, 1978) indicated that it is probably impossible to select a single sampling method for the total range of potential organic contaminants in air. A similar situation may arise when one samples workplace or ambient air at coal-gasification pilot plants. For example, methods that work well for the collection of C₂-C₆ hydrocarbons fail when applied for C₆-C₂₀ hydrocarbons. The less volatile C₆-C₂₀ hydrocarbons may be efficiently but irreversibly adsorbed. In contrast, a method that traps higher molecular weight hydrocarbons efficiently will allow the more volatile hydrocarbons to "break through" and be lost. Some methods are excellent for collecting hydrocarbons adsorbed to particulates but fail to retain vapor-phase organics. In summary, three distinct choices are possible: sampling for particulates; sampling for vapor-phase organics from C₁ to C₆; sampling for vapor-phase organics >C₆. From a public or employee health point of view, the first class, containing respirable particulates and the last, into which most of the known carcinogens fall, are the important classes to consider while sampling.

Concurrent with the selection of a method for collecting hydrocarbons from the air is the selection of a compatible method for extracting the collected organics from the sample matrix.

The selection of a method for identifying or quantifying the organics in an air sample will relate to the compounds of interest. Mere identification or confirmation of the presence of selected compounds such as benzapyrene may be performed using ultraviolet or fluorescent spectroscopy, or packed-column gas chromatography. Identification of a broad range of unknown hydrocarbons, however, requires sophisticated detection equipment such as high resolution, computer controlled, gas chromatography/mass spectrometry (GC/MS). These more complicated, more sensitive analytical methods cannot be applied to routine, large-scale analyses. In general, the simpler methods provide the least information.

A dichotomy exists between the published works of scientists interested in sampling for air pollution and scientists interested in the occupational hygiene field. Articles appearing in the public health and occupational

safety journals that relate to sampling of workplace air nearly always deal with the collection and analysis of a single hazardous compound or a few members of a class of closely related compounds. In contrast, articles in the literature of air pollution research appear to be the work of scientists, connected with governmental air monitoring agencies or with universities, who are generally interested in multicomponent analysis of atmospheric contaminants.

1.2 OBJECTIVES OF STUDY

A prime purpose of this study is to present as completely as possible a summary of the methods and findings of other researchers involved in sampling workplace air or in conducting air pollution studies. With this information in hand, one can eliminate repeating the work of others when developing a sampling program and can avoid methods that have been shown to have serious drawbacks.

The primary concern will be to identify those airborne organic compounds that could be hazardous to the workers who operate and maintain coal-conversion facilities. Sampling should include organic chemicals in the vapor phase as well as those adsorbed on respirable particulates. A suitable sampling unit must retain both vapors and particulates. Such a unit may require a dual sampler consisting of a particle filter backed up by a solid adsorbent for vapors. This arrangement is adaptable to either portable, personal, or stationary high-volume sampling. The intensity of concentrations of the pollutant encountered in the coal-conversion facility will determine the choice of sampling unit.

2 METHODS FOR COLLECTING SAMPLES

2.1 PARTICULATE MATTER AND PARTICULATE SORBED ORGANICS

2.1.1 High-Volume Air Sampling for Particulates

A high-volume air sampler is a device capable of pulling a large volume of air, at a known rate, through a filter, usually a glass or quartz fiber. Typical flow rates would be in the 40-125 m³/hr range according to such sources as the American Public Health Association (APHA, 1977), Bunn et al. (1975), and Cautrels and Van Cauwenberthe (1977). Along with the latter two sources, another report of this method being used for general sampling of hydrocarbons in urban atmospheres is Mendenhall et al. (1978); and for polynuclear aromatic hydrocarbons (PAH) in coke-oven emissions, Harrison and Powell (1975). However, Pupp et al. (1974) have warned that some PAHs have sufficient vapor pressures that losses may occur from the particulates that are trapped on the filter. Richard Kuppel of NIOSH, Cincinnati (personal communication, 1979), too, has indicated that this may be true for chrysens and pyrene trapped on personal air sampler filters. The American Public Health Association lists two tentative methods for high-volume air sampling of PAHs on atmospheric particulates (methods 11104-01-69T and 11104-02-69T, APHA, 1977). The obvious advantage of high-volume air sampling is that the concentration factor is very large, allowing for analysis of compounds that are present at the nanogram/m³ (ppb) level.

2.1.2 Low-Volume Air Sampling for Particulates

In contrast to the high-volume air sampler, which is a large stationary instrument, the low-volume (≈ 0.125 m³/hr) air sampler is a "personal sampler" that can be carried by a worker as he performs his duties. The typical personal sampler is described in the NIOSH Manual of Analytical Methods (methods #183, 184, 186, and 251 in NIOSH, 1977a) in sections that show methods for collection and analysis of PAHs in air. The sampler consists of a plastic holder containing a 37-mm glass fiber filter backed with a 37-mm, 0.8-micron pore size, silver membrane filter. A small battery-powered pump, capable of drawing through a minimum of 2 L/min is connected to the unit. The prescribed sampling period is 4 hr and the total volume that can be measured by this method depends upon the analytical methods used following collection of the sample. For mixed PAHs the minimum quantifiable amount is 2 g/m³ air sample. The personal sampler has the obvious advantage that the sample it obtains is more representative of what the worker is exposed to than is the one obtained by a stationary sampler.

2.2 VAPOR-PHASE ORGANICS

2.2.1 Direct Collection

Direct collection and injection of air samples into a GC is not practical at the concentrations normally encountered in the industrial atmosphere.

Grob and Grob (1971) estimated that collecting 0.1 μg of a compound present in the atmosphere at 0.1 ppb on a capillary GC column would require 4 hr of sampling at a rate of 8 mL/min. Except in a dangerously polluted atmosphere, the amount of air sample that would have to be injected into a GC column to collect sufficient material for analysis is far too large to be compatible with the system. Some method for preconcentrating the sample is required.

2.2.2 Cryogenic Trapping

A direct method for concentrating the pollutants in the air is cryogenic trapping. The principle of cryogenic trapping is quite simple. The air being sampled is drawn through a glass or metal tube that is suspended in liquid nitrogen, liquid oxygen, or dry ice and acetone. The volatile materials in the air condense upon the walls of the tube and remain there while the air passes on through.

Cryogenic trapping is perhaps the best method for collecting such very volatile hydrocarbons as methane. Most hydrocarbons below C_6 are poorly retained on solid adsorbents such as Amberlite XAD or Tenax at normal air temperatures. However, this method also poses problems. Partial loss of the sample may occur if a microfog is produced in the trap (Kaiser, 1973). (Part of the sample may pass through instead of condensing on the walls of the trap.) Kaiser overcame this problem by filling the trap with a solid adsorbent. Water vapor in the air sample can form ice and may plug the trap or interfere in the analytical procedure (Westberg et al., 1974; Perry and Twibell, 1973). The inclusion of a drying agent in front of the trap can eliminate such ice formation; Westberg et al. (1974) used K_2CO_3 in the drying cartridge. Russell and Shaddoff (1977) investigated the use of partially dehydrated salts to remove water from halocarbon contaminated air. Only partially dehydrated MgSO_4 absorbed water without also adsorbing the hydrocarbons.

The usefulness of cryogenic sampling both by itself and in combination with solid adsorbents, has been demonstrated. Westberg et al. (1974) sampled the urban air of both Houston and Phoenix for light hydrocarbons ($\text{C}_2\text{-C}_6$). Cudney et al. (1977) and Kaiser (1973) used cryogenic tubes packed with solid adsorbents to trap $\text{C}_1\text{-C}_6$ hydrocarbons. The last two cases are difficult to classify as either cryogenic or solid adsorbent systems because they had elements of both.

2.2.3 Collection on Solid Adsorbents

2.2.3.1 Activated Carbon

Activated carbon (charcoal), with its very large surface area to mass ratio, is an excellent adsorbent material. Due to its inclusion in the NIOSH Manual of Analytical Methods (1977a) and the ready availability of low cost, disposable sampling tubes, activated carbon is widely used to extract and concentrate pollutants from air. Acrylonitrile, pyridine, benzene, octane, and pentane are examples of a few of the compounds that NIOSH recommends be collected on activated carbon. The NIOSH trap consists of a two-

section activated carbon filter. The inlet filter contains 100 mg of activated carbon and is backed by a second filter containing 50 mg of activated carbon. The tube is sealed at both ends until used. After the required sample has been drawn through the tube, both sections are broken apart, extracted, and analyzed. If the concentration in the 50-mg section exceeds 10-25% of the amount in the 100-mg section, too large a sample was taken and the sample is thrown out. A smaller volume of air is sampled with a new tube. Similar filters have been used by Grob and Grob (1971) and Burghardt and Jeltet (1975) in their general hydrocarbon studies of urban atmospheres.

As with other methods, the use of charcoal traps has some disadvantages. Humidity is a critical factor. Under humid conditions the breakthrough volume (air sampling capacity) is markedly decreased (NIOSH, 1977a). Some organic compounds are bound irreversibly and others are recovered only with difficulty (Leinster et al., 1977). Despite these difficulties, carbon has been shown to be an effective trap for hydrocarbons. Grob and Grob (1971) were able to recover and identify more than 100 organic compounds from urban air using a two-section charcoal trap.

2.2.3.2 Polymeric Resins and Chromatographic Adsorbents

Most of the recent work on air pollutant sampling concerns the use of polymeric resins, which have a high affinity for trace organic compounds and a low affinity for water. These may be divided into two basic types, thermally stable resins that do not decompose at temperatures below 300°C, and resins that do not dissolve when exposed to common organic solvents. Tenax GC and the Chromosorb series are examples of thermally stable polymers. The XAD resins and chromatography packings such as Poropak N and Q are examples of chemically stable polymers. The choice of which type to use is determined by the method that will be used to recover the adsorbed organics, i.e., thermal desorption or solvent elution.

Many articles in the recent literature show the successful use of both types of adsorbents. Tenax GC (2, 4-diphenylparaphenylene oxide polymer) has been used by Bertsch et al. (1974), Gallant et al. (1978), Pellizzari et al. (1976 a,b) and Russel (1975) for sampling urban air samples and in laboratory tests, versus other polymers. Both Russel (1975) and Pellizzari et al. (1976b) found it to be superior to the other adsorbents they tested, including carbon, Poropak N, Poropak R, Chromosorb 104, and Carbosieve B. Mieure and Dietrich (1973) describe using Tenax GC to collect the odor-causing organic compounds responsible for "new car odors and [the aroma of] freshly ground coffee." Chromsorb 102 has been used by Perry and Twibell (1973), and Mendenhall et al. (1978) used Chromosorb 102 as packing in a cryogenic trap to collect C₂-C₆ hydrocarbons. Pellizzari et al. (1976b) compared Chromosorb 104 to Tenax GC but preferred the latter adsorbent polymer. Mieure and Dietrich (1973) recommended using Chromosorb 101 for acidic and neutral organics and Chromosorb 105 for low boiling components in air sampling.

A styrene divinylbenzene polymer (XAD-2) has frequently been used to remove organics from water but only recently has it been applied to air sampling (Bunn et al. 1975). In the Bunn et al. study, Kansas City air was sampled by using Tenax GC and XAD-2. The same components, identified by GC/MS, were observed in both samples. Gallant et al. (1978) compared the

breakthrough volumes for Tenax GC and XAD-2 and found them comparable. Anders Andren, University of Wisconsin, Madison, Water Chemistry Program (1978, personal communication) has used XAD-2 resin in a back-up trap in a commercial high volume particulate sampler to recover PCBs and PAHs that passed through the glass fiber filter. Kuppel of NIOSH (personal communication, 1979) is experimenting with a solvent extractable resin similar to XAD-2 as a backup for the 37-mm glass fiber and silver membrane filter used in the NIOSH low-volume personal sampler.

Poropak N and Poropak Q are liquid chromatography phases that have been used to collect halogenated hydrocarbons (Russel and Shadoff, 1977). Pellizzari et al. (1976b) compared the breakthrough volumes and collection efficiencies for 12 compounds collected on several different adsorbents, including Tenax GC and Poropak A. The collection efficiencies were 100% for both polymers, and breakthrough volumes were similar.

2.2.3.3 Miscellaneous Adsorbents

A few other materials that do not fall into the previous categories have had limited use in air sampling. Kaiser (1973) used a molecular sieve in a gradient cooled (-20 to -160°C) trap to collect C₁-C₄ hydrocarbons from traffic air. Pellizzari et al. (1976b) found Carbosieve B to be less satisfactory than Tenax GC for general hydrocarbon analysis. Kaiser (1973) also used Dexsil 300 GC on Chromosorb AW DCMS, a GC column packing, to concentrate organics from compressed cylinder air. Silica gel traps similar to the carbon traps described in Section 2.2.3.1 have been used to trap basic organic contaminants, such as ethylamine, xylidine, and n-ethylmorpholine from air (Wood and Anderson, 1975; NIOSH, 1977a). Turner and Glotfelty (1977) described a sampler using porous foam plugs capable of efficiently trapping the pesticides trifluralin and heptachlor. Since foam plugs have been routinely used to trap chlorinated hydrocarbons from water, it is likely that other organic compounds would also be removed from air.

3 METHODS FOR RECOVERING TRAPPED ORGANICS FROM FILTERS OR SOLID ADSORBENTS

3.1 SOLVENT EXTRACTIONS

3.1.1 Direct Extraction

Direct solvent extraction, in which a solvent is simply added to or passed through a trapping agent, is a common procedure when small amounts of adsorbent and small volumes of solvent are used. The NIOSH (1977a) methods use charcoal samplers and a direct elution with CS_2 to desorb organics from carbon filters. Grob and Grob (1971) used a microrefluxing unit to facilitate desorption. Both NIOSH (1977a) and Wood and Anderson (1975) describe methods for collecting aromatic amines on silica gel with subsequent desorption of the amines by using ethanol. Bunn et al. (1975) used methylene chloride to elute trapped organics from XAD-2 resin.

3.1.2 Soxhlet Extraction

Soxhlet extraction is often used when large amount of adsorbent must be extracted. High-volume air sampling filters are usually 8 x 10" and would require the use of an excessive volume of solvent if sample was extracted from the entire filter in one step. Bunn et al. (1975), Cautrels and Van Cauwenberghe (1977), and Hill et al. (1977) used Soxhlet extraction to desorb organics from glass fiber filters. Solvents used in the process include benzene, cyclohexane, methanol and methylene chloride. Turner and Glotfelty (1977) extracted chlorinated hydrocarbons from foam plug absorbers in Soxhlet extractors. One disadvantage of this method is the need for reducing the solvent volume before the Soxhlet extract can be further processed or analyzed.

3.1.3 Ultrasonic Agitation

Effective solvent desorption of organic pollutants from the trapping agents requires intimate contact between the solvent and adsorbent material. The NIOSH (1977a) methods for PAHs in air, nos. 183 and 184, and total particulate aromatic hydrocarbons, no. 206, all describe a procedure that uses ultrasonic agitation. The glass fiber filter, together with either benzene or cyclohexane, is placed in an ultrasonic bath and vigorously agitated for a few minutes. For the PAHs, recoveries of internal standards ranged from 95 to 98%. This method requires only a small fraction of the time required for Soxhlet extraction.

3.1.4 Choosing an Elution Solvent

The primary concerns in choosing a solvent for recovering sorbed organics from a sampling unit are solvent toxicity, quantitative recovery of sorbed organics, and the presence of interferences that would affect subsequent analysis. Both benzene and carbon disulfide are very toxic and require

special precautions for safe use. A few comparisons have been made to determine relative solvent effectiveness for extracting particulate organics from glass fiber filters. Hill et al. (1977) preferred to use methanol to extract glass fiber filters because it is less toxic than benzene and recovers more compounds than cyclohexane. Cautrels and Van Cauwenberghe (1977) used successive Soxhlet extractions with benzene and methanol. The inorganic matter may be eliminated by washing the extract with water. If visible or ultraviolet spectroscopy is used to identify unknowns, the solvent must not absorb light strongly in the same regions as the unknown compounds absorb light. If gas chromatography is used, the retention time for the solvent and unknowns must be different.

3.2 THERMAL DESORPTION

Thermal desorption is a common procedure for removing trapped organic chemicals from Tenax GC or the Chromosorb series of resins. After the sample has been collected on the resin, the resin adsorbent tube is connected to a cool or cryogenic gas chromatography column. The resin adsorbent tube is heated while the tube is being flushed by a clean, inert gas. The pollutants are swept out of the resin tube into the head of the cold GC column where they are trapped again. The GC column and sample are then ready for a normal GC run.

Tenax GC has been used by Bertsch et al. (1974), Bunn et al. (1975), Mieure and Dietrich (1973), and Pellizzari et al. (1976 a,b) in various studies of hydrocarbons in urban air. In each case, the Tenax GC traps were thermally desorbed onto a GC column in a cryogenic (-40 to -50°C) GC oven. Cudney et al. (1977), Mendenhall et al. (1978), and Perry and Twibell (1973) performed similar studies in which Chromosorb 102 was the trapping agent. Mieure and Dietrich (1973) used Chromosorb 101 and 105 for trapping organic chemicals from air and used thermal desorption to recover the pollutants.

The thermal desorption method, like the solvent extraction method, has drawbacks. Mieure and Dietrich (1973) warn that care must be taken to desorb the sample below the decomposition temperature of the resins. There is some concern that the elevated temperatures needed to desorb high molecular weight compounds such as PAHs may cause decomposition or rearrangement. Dale Felix of Battelle PNL (personal communication, 1978) reported losses, decomposition, and non-reproducible results when using Tenax GC, and he preferred to use XAD-2 resin for sampling hydrocarbons in air. Kuppel of NIOSH (personal communication, 1979) warned that PAHs are reactive and that there is no assurance that molecular rearrangements do not occur during desorption of Tenax GC.

4 METHODS FOR IDENTIFYING AND QUANTIFYING THE RECOVERED ORGANICS

4.1 SPECTROSCOPIC METHODS

Polynuclear aromatic hydrocarbons (PAHs), a class of organic compounds containing many known carcinogens that are of particular concern to air pollution chemists and occupation health scientists, may be detected by adsorption of ultraviolet light or by fluorescence. These properties are the basis for the NIOSH (1977a) methods for identifying total particulate aromatic hydrocarbons in air (method #206) and PAHs in air (methods #183, 184, 186). The four methods are similar except for the procedures used to separate individual compounds in the samples. Each of these separations requires the use of different chromatography, namely, preparative gas, column, thin layer, or the high-performance liquid type. The APHA (1977) suggests similar procedures for the analysis of PAHs in air, coke-oven emission, and auto exhaust. The sample is first separated by one of the above procedures then quantified by ultraviolet or fluorescence spectroscopy. Waters Associates (1977) describe HPLC methods in which dual ultraviolet detectors of different wavelengths or an ultraviolet and fluorescent detector pair are used. The absorbance ratio or absorbance to fluorescence ratio is a characteristic of each PAH and may be used to confirm the identity of a sample PAH. The minimum detectable amount for the most sensitive of these methods, HPLC, is at the subnanogram levels on the HPLC column (Waters Associates, 1977). Separation of sample components using column chromatography or GC with fraction collection requires a sample size of from a few micrograms to a submilligram.

4.2 GAS CHROMATOGRAPHY

Gas chromatography (GC) has been widely used for separation and detection of organic compounds in air samples. For convenience the GC methods have been grouped into three sections, conventional packed column GC, capillary column GC, and gas chromatography/mass spectrometry (GC/MS).

4.2.1 Packed Column GC

The majority of the methods in the articles mentioned in the previous sections use some form of gas chromatography for separation and identification of hydrocarbon samples. The GC is almost universally available in analytical laboratories and is an excellent tool for separation and identification of organic compounds. Conventional packed GC columns are usually 1/16-1/4" ID and 20' or less in length. A choice of hundreds of different column packing materials is available. Column packings and operating conditions are too numerous to be mentioned here.

General hydrocarbon analyses have been performed by Burghardt and Jeltres (1975), Hill et al. (1977), Kaiser (1973), Mendenhall et al. (1978), Perry and Twibell (1973), and Westberg et al. (1974) on conventional gas chromatographs equipped with flame ionization detectors. Unknowns are identified by comparing the retention time of the unknown to that of standards.

Confirmation may be accomplished by analyzing the same sample on two dissimilar GC columns. Turner and Glotfelty (1977) used a gas chromatograph equipped with an electron capture detector to detect halogenated hydrocarbons in air extracts. This type of detector is far more sensitive to halogenated hydrocarbons than the flame ionization detector, but is rather insensitive to nonhalogenated hydrocarbons.

The gas chromatograph is well suited for attaching to the thermal desorption equipment used for resins such as Tenax GC or the Chromosorb series. The resin may be desorbed directly onto a cold GC column, concentrating the sample into a small "plug" at the beginning of the column (Mendenhall et al., 1978; Bunn et al., 1975; Bertsch et al., 1974; Pellizzari et al., 1976 a,b). The GC column and oven are then heated and a normal GC separation takes place.

4.2.2 Gas Chromatography/Mass Spectroscopy (GC/MS)

The combination of GC with MS is very useful for complex samples because identification and confirmation can be carried out in one operation. The operation is not routine and the equipment is costly, particularly when the GC/MS is interfaced with a computer. This system is ideal for dealing with complex environmental samples.

Mendenhall et al. (1978) and Bunn et al. (1975) combined the use of gas chromatography and mass spectroscopy in their studies of urban air. Russel and Shadoff (1977) combined electron capture detector GC with MS to identify halocarbons in the air near Midland, Michigan.

4.2.3 Capillary Column GC/MS

A further refinement of GC/MS is to use capillary columns to separate the organic components. Capillary columns with lengths up to 120 meters (400 ft) have been used to separate hydrocarbons (Grob and Grob, 1971; Pellizzari et al., 1976 a,b). Capillary columns provide very high resolution, are able to separate similar compounds, and need only small amounts of sample. Grob and Grob were able to separate and identify 108 samples in an extract from the air of Zurich, Switzerland. This is the most sensitive method among those described. It is also the most tedious and expensive.

4.3 PREPARATION OF STANDARDS AND ASSESSMENT OF EXTRACTION AND SAMPLING EFFICIENCIES

The calibration of air sampling systems is one area of air pollution research that needs further consideration. Some scientists do not measure the collection efficiencies of their air sampling systems (Mieure and Dietrich, 1973; Bunn et al., 1975). The results they report are minimum, rather than actual, concentrations for organics in air. In many of the experiments reported in this paper, only qualitative information was obtained. Standards were used to confirm the identity of an unknown but not to measure its amount.

Perhaps the simplest method for calibration is to add an internal standard to a sample during the extraction sequence. Several of the NIOSH (1977a) methods use this approach. During or following the desorption step, a compound chemically similar to those being analyzed is added to the desorption solvent (methods #183, 184, and PAHs). In other cases, the actual compound is added to a separate tube and carried through an identical procedure (method #127 for organic solvents). Neither method measures adsorber efficiency. Those NIOSH methods using adsorption tubes require the use of dual section tubes. If none, or only a small fraction of the sample, is found in the back-up portion of the tube, the sampling efficiency is assumed to be quantitative.

The best procedure for estimating sampling (collection and extraction) efficiency consists of adding a model compound to the airstream as it is sampled. Three such procedures have been described in the recent literature. Burghardt and Jeltres (1975) used open diffusion from a liquid to prepare calibration mixtures. NIOSH (1977b) prepared calibration standards for validation tests by using a special syringe. Calibration liquids were injected into a clean gas stream at a known, reproducible rate.

The third procedure uses Teflon permeation tubes. The liquid or liquefied gas is contained in a tube made of Teflon or Teflon joined to a stainless steel reservoir. The rate of diffusion of the standard through the Teflon is constant if the temperature and pressure of the system are kept constant. The permeation rate may be determined by repeated, accurate weighings of the Teflon tube or Teflon coated stainless steel container. Burg (1976), Saltzman et al. (1971), and Scaringelli et al. (1970) have used permeation tubes to prepare calibration gases for vinyl chloride or low molecular weight hydrocarbons. Dietz et al. (1974) described an improved system that allowed tanks of gas to be used as a gas source. They also devised a pressure differential method for rapid determination of the permeation rate. Pellizzari (1978) prepared permeation tubes using a number of common organic solvents. Both Teflon and polyethylene were used to contain the organic liquids. Permeation rates were faster when polyethylene was used. The permeation tube concept could be extended to less volatile standards if the permeation tube were heated above room temperature.

A rather novel method for laboratory calibration of air sampling equipment has been suggested by Andren of the Univ. of Wisc., Madison, Water Chemistry Program (personal communication, 1978) in which a GC equipped with an effluent splitter is used to deliver a precisely measured amount of standard to the sampler. The standards are injected into the GC and measured by the detector output while the split portion (10:1) goes to the sampling unit.

5 RECOMMENDED ANALYTICAL PROCEDURES FOR SAMPLING AND ANALYZING WORKPLACE AIR AT COAL-CONVERSION FACILITIES

The specific requirements for sampling of workplace air at coal-gasification pilot plants have produced a recommended procedure that differs markedly from the standard high-volume air sampling procedure. A principal requirement is that only explosion proof equipment be used, since there is the potential that sampling would occur in an explosive atmosphere. In addition, the sampling device must be capable of nearly quantitative capture of both vapors and particulate matter, while preserving the integrity of the sample to the highest degree possible.

The sampling train that was chosen consists of a Teflon filter followed by a bed of Amberlite XAD-2 resin. This system permits collection of a large enough sample so that multiple analyses may be performed on a single sample. Fractionation of the sample into chemical classes of compounds is also possible. The alternate choice of a resin, Tenax, is suitable for collecting a single analysis sample because the entire sample is consumed during the analysis.

5.1 MATERIALS AND EQUIPMENT

The intention in designating an experimental procedure is to use commercial equipment with a minimum of modification, so that others can readily adapt these methods to their own needs. With the exception of the custom built air sampler, all equipment is of a common, commercially available design. The sources for equipment listed below indicate the suppliers from whom the equipment and materials were purchased for use in the initial testing of the experimental procedure. This list is not to be construed as an endorsement of these products or suppliers by the author, by Argonne National Laboratory, or by the U.S. Department of Energy.

5.1.1 Materials

All solvents used in the extraction procedure are high purity, distilled-in-glass grade and are used as received from the suppliers (Waters Associates, Milford, Mass., Burdick & Jackson, Muskegon, Mich., Fisher Scientific Co., Itasca, Ill.). Amberlite XAD-2 resin (Mallinckrodt Chemical Co., St. Louis, Mo.) is subjected to exhaustive extraction and drying before use. Fluoropore 76 mm (3") Teflon filters having a nominal 0.3 μ pore size are used to filter particulate matter (Ghia Corp., Pleasanton, Calif.).

5.1.2 Equipment

Soxhlet extractors (Fisher Scientific Co.) are used to extract the samples from the filter and the XAD resin. Kuderna-Danish evaporative condensers are used to reduce sample volumes, minimizing loss of the sample. Hewlett-Packard 5840A or 5880A gas chromatographs equipped with 50M flexible silica capillary columns and either flame ionization detectors or the mass spectrometer are used to identify and quantify the compounds. A Hewlett-Packard 5980A Mass Spectrometer coupled to a 5840A gas chromatograph and a 21

MX computer are used to obtain mass spectra and to manipulate data. The explosion proof air sampler (Figs. 5.1 and 5.2) has been fabricated by the Argonne Glass Shop and Central Shops metalworking facility. The unit incorporates an Amatek Model S14586 explosion proof vacuum motor (Amatek, Kent, OH), and in-line Gilmont flow meter (Precision Scientific, McGaw Park, Ill.) with ranges from 0.2-36.0 L/min; and a glass and stainless steel filter and resin chamber. Glass joints were obtained from Ace Glass Co. (Vineland, N.J.). The motor housing is not commercially available and must be custom built. The air sampler is housed in the shell from a Precision Scientific Co. Model 63083 High Volume Air Sampler (Fisher Scientific Co., Itasca, Ill.) to protect the filter from rain and dust.

5.2 SAMPLING AND ANALYTICAL PROCEDURES

5.2.1 Preparation of Amberlite XAD-2 Resin

The adsorbent resin is received moist from the supplier and must be precleaned to remove water and contaminants that interfere with analysis of the trapped organics. The resin is dried to 100°C and successively extracted with absolute alcohol, acetone, and methylene chloride for 4-hr periods. The resin is again dried for a 24-hr minimum at 100°C and stored in glass containers until used. A test batch of cleaned resin produced no objectionable interferences when Soxhlet extracted with methylene chloride according to the same procedure was used to extract the samples.

5.2.2 Collection of Samples

The principal changes that differentiate this collection method (Fig. 5.3) from the traditional high-volume air sampling procedure are: the volume of air sampled is smaller; a resin bed is included so that vapors in the air sample are trapped; and the physical size of the filter is greatly reduced. The addition of a resin bed in the air path reduces the maximum flow rate through the filter from 2000 to approximately 600 L/min. An 8 x 10" glass fiber filter is generally used in the high-volume air sampler. This filter is difficult to work with because it may not be folded for weighing, it is hygroscopic, and it has repeatedly been implicated as the cause for changes in composition of the sample. Pitts et al. (1979) and Lee (1979) reported significant changes in the composition of polycyclic organic matter collected on glass fiber filters from polluted air containing NO₂ and O₃. The 8 x 10" glass fiber filter has been replaced by a 76-mm (3"D) porous Teflon filter that has a nominal 0.3 μ pore size. Beneath the Teflon filter is a bed containing 120 g (~300 mL) of XAD-2 resin. The entire Teflon filter may be extracted in a standard sized Soxhlet extractor. The use of 120 gm of XAD-2 should allow for the collection of a 3-hr sample before breakthrough and loss of sample occurs. A variable transformer may be used to control the motor speed and vary the flow through the filter.

The sampling unit is assembled with a weighed, 76-mm Teflon filter in place and 120 g of XAD-2 resin in the chamber beneath the filter. The motor is started and the voltage to the motor is adjusted so that the desired flow, measured on the in-line flowmeter, is achieved. After sufficient sample has

Fig. 5.1. Explosion-Proof Air Sampler

Fig. 5.2. Modified Air Sampler with Explosion-Proof Motor, Cross-Sectional View

Fig. 5.3. Collection and Analysis Scheme for Sampling of Workplace Air at Coal Conversion Facilities

been collected the sampler is stopped, disassembled, and the resin and reweighed filter are transferred to Soxhlet extractors.

5.2.3 Extraction Methods

Soxhlet extraction with methylene chloride (CH_2Cl_2) has been chosen for removing trapped organics from the porous Teflon filters or the XAD-2 resin. In this method, the sample is rinsed repeatedly with a bath of freshly distilled solvent and the extract is concentrated in a relatively small amount of solvent. Methylene chloride was chosen because it is an excellent general organic solvent, particularly for aliphatic and aromatic hydrocarbons. It also has a low boiling point, thus it does not require high temperatures for extraction or for subsequent solvent removal, lessening the possibility of degrading labile compounds in the extract. Extraction times must be kept as short as possible consistent with recovery of the sample. Some resin is

extracted along with the sample. Long extraction times can produce significant interferences from breakdown products of the styrene divinylbenzene, XAD-2 resin.

5.2.3.1 Extraction of Porous Teflon Filters

The porous Teflon filters are removed from the sampler, weighed, and placed in the extraction thimble of a Soxhlet extractor. One hundred-fifty milliliters of distilled-in-glass methylene chloride (CH_2Cl_2) is added to the extraction flask and the extraction is carried out for 2 hr. The extract is removed, a new batch of solvent is added, and the process is repeated for an additional 0.5 hr. The extracts are combined, placed in a Kuderna-Danish evaporator, and the volume of the extract is reduced to a few milliliters.

5.2.3.2 Extraction of XAD-2 Resin

Extraction of XAD-2 resin is carried out in a manner similar to that for the filters. The resin is placed in a glass extraction thimble and extracted twice with fresh solvent. Up to 40 gm of resin may be extracted at once in a standard 33 x 80 mm extraction thimble. Larger extractors are available, but they require larger volumes of extracting solvents. Larger quantities require extraction in separate batches. The resin is recleaned, dried, and stored for reuse.

5.2.4 Identification and Quantification of Organic Compounds in the Extracts

A combination of gas-chromatography (GC) and gas chromatography/mass spectrometry/computer (GC/MS/comp) is used to analyze the samples.

Those compounds for which standards are available may be identified and quantified by the use of capillary column gas chromatography. Most of the remaining compounds present in a sample are identified by GC/MS using comparisons of mass fragmentograms to spectral libraries that contain the mass fragmentograms of thousands of different chemicals. Semiquantitative estimates, good to within an order of magnitude or better, can be made for those compounds in a sample for which no standards are available. The total ion chromatogram from the GC/MS can provide an "area" or total ion count similar to the peak area of the GC detector output. A total ion count is made by summing all the ions produced by a compound when it is fragmented in the GC/MS. One assumes that for similar compounds, equal quantities of the compounds produce equal numbers of ions in the mass spectrometer. Instead of comparing the total ion count of a compound to a standard of that same compound, the comparison is made to a standard of a closely related compound that may be commercially available.

6 CALIBRATION OF THE SYSTEM, ESTIMATES OF THE MAXIMUM RECOVERY ACHIEVABLE BY THIS METHOD

6.1 SAMPLE LOSS ASSESSMENT

6.1.1 Losses Due to the Solvent Reduction Step

In order to perform Soxhlet extraction on large amounts of XAD-2 resin (≈ 120 g), sizable quantities of solvent must be used. The sample becomes dissolved in approximately 0.3 L of CH_2Cl_2 . The sample size must be reduced to a few milliliters before GC analysis can be done. This solvent reduction step can result in significant losses of the more volatile components in the sample. A simple experiment was devised to measure the losses that could be expected in this step.

Several common, moderately volatile aromatic compounds were chosen for the test. Standard solutions containing toluene, ethylbenzene, o-xylene, and naphthalene were prepared. An aliquot of the standard was dissolved in 0.5 L of CH_2Cl_2 and transferred to a Kuderna-Danish evaporator, and the solvent was reduced to a volume of approximately 4 mL. The recovered standard was diluted to a suitable volume and compared by GC to a second aliquot of the original standard. If careful attention is paid to the rate at which the solvent is boiled off and the solvent reduction is stopped before all of the CH_2Cl_2 has been driven off, nearly uniform recoveries of 89-90% is achieved. Therefore, losses of up to 10% might be expected even under carefully controlled conditions.

6.1.2 Losses Due to the XAD-2 Resin or Extraction Step

The XAD-2 resin used in the vapor trap has two distinctly different properties regulating the amount of materials that can be adsorbed by the resin. One is a weight capacity. The XAD-2 resin can adsorb approximately 10% by weight if no air flow passes through it. This value ordinarily would not be exceeded in sampling any nonexplosive industrial atmosphere. However, when air is passed through the XAD-2 resin bed, the resin acts like a chromatography column. The sample gradually moves through the bed and eventually passes out the exhaust end of the sampler. This limit, called the specific retention volume, indicates how much air can pass through the column before the sample is swept away and lost. It is a temperature dependent value. The higher the temperature, the lower the specific retention volume. Some typical examples of specific retention volumes, at 20°C (68°F), for compounds used to test the resin are 258 L/g for toluene and 564 L/g for ethyl benzene (Harris et al., 1979). In general, within a chemical class, the volume increases as the boiling point increases.

To properly test the air sampler it is desirable to prepare a "standard air sample" approximating one taken in a real workplace. A constant rate syringe was built so that a uniform, low level contaminant could be metered into the air stream entering the sampler. The syringe delivers a standard solution to a small heating block suspended in the air stream above the

sampler where the solution is rapidly vaporized and mixed with the air. By changing the syringe size and composition of the standard solution, it is possible to vary the level of contaminant from a few parts per billion to a few parts per million.

Breakthrough tests were conducted using a standard, nonexplosion proof high-volume air sampler, fitted with an auxiliary stainless steel holder for the XAD-2 resin. This holder was positioned beneath the place where the 8 x 10" glass fiber filter is normally positioned and was in line with the total air stream. A solution containing 1.5 mg of toluene, o-xylene, and naphthalene was slowly evaporated in the air stream over the resin bed. No glass fiber filters were used during the calibration runs. The air flow was set at 24 cfm (680 L/min). Short sampling times (i.e., smaller total volumes of air sampled) and larger amounts of resin were found to improve the percentage recovery. Table 6.1 shows the effect of decreasing the flow rate and shortening the sampling time. All tests were made using 120 g of XAD-2 resin.

Table 6.1. Recovery of Volatile Organic Compounds from Spiked Air Sample Using XAD-2 Resin

Sampler	Sampling Time (min)	Flow Rate (LPM)	% Recovery		
			Toluene	o-Xylene	Naphthalene
Nonexplosion proof	205	680	19	42	54
Nonexplosion proof	85	680	33	66	88
Explosion proof	64	35	96	96	93
Explosion proof	105	30	97	94	101

7 SUMMARY AND CONCLUSIONS

A sampling methods and analytical procedure has been described for the determination of particulate and organic contaminants in coal-conversion facilities. Since it was not possible to select a single method to determine the total range of possible contaminants, a modified technique has been developed that enhances the determination of organics $>C_6$ present on particles and in the vapor phase. The technique was also selected for its potential to collect large samples for further experimentation and for its potential ultimate sensitivity.

The technique differs from traditional high-volume sampling and personal monitoring for airborne hazards. The apparatus constructed uses an explosion-proof vacuum motor to draw an air sample through a particulate filter in series with a sorbent bed of XAD-2 resin. The sample is collected at a medium-volume sampling rate, and the organics are extracted from the filter and resin and subsequently identified and quantified by computer-controlled, capillary column GC or GC/MS. The sampling technique has been tested in a laboratory apparatus for several model compounds with good results.

The capabilities of the sampler will be tested further in a variety of laboratory and field experiments for the broad range of organics found in coal-conversion facilities. The resin bed will be used to collect samples of suitable magnitude from the workplace environment such that further experimentation such as bioassay can be performed.

ACKNOWLEDGMENTS

Thanks are due to Paul Cunningham, Joseph Stetter, Sidney M. Gordon, Leo Raphaelian, and Kenneth Wilzbach for review of this manuscript, and Wyman Harrison for his many helpful suggestions in this research project.

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APPENDIX

Abstracts of Reports Concerning the Sampling and Analysis
of Trace Organics in Air

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TITLE: The Determination of Organic Volatiles in Air Pollution Studies:
Characterization of Profiles

AUTHORS: Bertsch, Wolfgang, Ray C. Chang, and Albert Zlatkis

PERFORMING ORGANIZATION: Department of Chemistry, University of Houston,
Houston, Texas

SPONSORING ORGANIZATION: NASA, Life Sciences Div., Houston, Texas

REPORT NO./JOURNAL: J. Chromatographic Sci. 12, 175-182 (1974)

NTIS/GPO No.: N/A

TYPE OF REPORT: Journal Article

Air samples were collected in the Houston, Texas, area, utilizing vapor samplers consisting of 4 mL of Tenax GC resin in an 8 mm ID x 110 mm-length glass tube. Silanized glass wool was used to contain the resin inside the sampling tube. The samples were collected thermally desorbed onto a cooled GC precolumn, and then analyzed by capillary column GC or GC/MS. The authors reported excellent recoveries for hydrocarbons with a chain length greater than C₆. Nearly 100 compounds were identified in one freeway air sample.

TITLE: Environmental, Health and Control Aspects of Coal Conversion:
An Information Overview

EDITORS: Braunstein, H.M., E.M. Copenhauer, and H.A. Pfuderer

PERFORMING ORGANIZATION: Oak Ridge National Laboratories, Oak Ridge, TN

SPONSORING ORGANIZATION: Energy Research and Development Agency

REPORT NO./JOURNAL: ORNL/EIS-94, ORNL/EIS-95

NTIS/GPO NO.: Vol. I - 1977 O-238-328, Vol. II - 1977 O-238-329

This massive two-volume test is an encyclopedia devoted to coal conversion. It has chapters on virtually every aspect of coal conversion. There are chapters concerning coal formation and composition, coal-conversion processes, and environmental effects of coal products on animals, humans, and plants. There are excellent descriptions of current coal-conversion projects. Process designs are described as well as product composition from each type of process. Extensive bibliographies are included with each chapter.

TITLE: Sampling and Characterization of Air for Organic Compounds
AUTHORS: W.W. Bunn, E.R. Deane, D.W. Klein, and R.D. Kleopfer
PERFORMING ORGANIZATION: Region VII Laboratory, U.S. Environmental
Protection Agency, Kansas City, Kansas 66115
SPONSORING ORGANIZATION: Region VII Laboratory, U.S. Environmental
Protection Agency, Kansas City, Kansas 66115
REPORT NO./JOURNAL: Water, Air, and Soil Pollution 4, 367-380 (1975)
NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Publication

The authors sampled both particulate and vapor-phase organics in Kansas City air. Eighty-two compounds were identified, including aliphatic, aromatic, and polyaromatic hydrocarbons. Three chlorinated hydrocarbons and 13 phenolic compounds were identified. Particulate samples were obtained by using a high-volume sampler containing an 8 x 10" glass fiber filter. Vapor samples were drawn through either XAD-2 or Tenax GC resins. Methylene chloride extractions were used to recover organics from the filters and XAD-2 resin. Tenax GC was thermally desorbed directly into a cool (40°C) GC column for direct analysis. Identification of the eluted compounds was made by using a conventional packed column GC/MS system.

TITLE: Use of Permeation Tubes for Calibration of Vinyl Chloride Analyses
AUTHORS: William R. Burg, Shelton R. Birch, John E. Cuddeback, and
Bernard E. Saltzman
PERFORMING ORGANIZATION: Department of Environmental Health, University of
Cincinnati, Cincinnati, Ohio 45627
SPONSORING ORGANIZATION: U.S. Environmental Protection Agency/National
Institute for Environmental Health Sciences
REPORT NO./JOURNAL: Environmental Science and Technology, 10(3), 1233-1237
(1976)
NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

This article presents the results of a series of calibrations for vinyl chloride in Teflon permeation tubes at three different temperatures (25°, 30° and 35°C) and for time spans of up to 235 days. A slow polymerization of the vinyl chloride within the tube was noted, resulting in a gradual, but predictable, decline in the permeation rate.

TITLE: Gas Chromatographic Determination of Aromatic Hydrocarbons
in Air Using a Semi-Automatic Preconcentration Method

AUTHORS: E. Burghardt and R. Jeltjes

PERFORMING ORGANIZATION: T.N.O. Research Institute for Environmental
Hygiene, Postbus 214, Schoemakerstraat 97,
Delft, The Netherlands

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Atmospheric Environment, 9, 935-940 (1975)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

A time programmable semi-automatic air sampler was devised that used absorbent charcoal to trap C₆-C₁₀ aromatic hydrocarbons from air samples. Carbon disulfide (CS₂) was used to elute the aromatic compounds from the charcoal adsorbent material. Analysis was performed by conventional packed column GC. Results are presented for several 2-hr air sampling sessions at various sites in the Netherlands.

TITLE: Fast Quantitative Analysis of Organic Compounds in Airborne
Particulate Matter by Gas Chromatography with Selective Mass
Spectrometric Detection

AUTHORS: W. Cautrels and K. Van Cauwenberghe

PERFORMING ORGANIZATION: Dept. of Chemistry, University of Antwerp (U.I.A.),
B-2610 Wilrijk (Belgium)

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Journal of Chromatography, 131, 253-264 (1970)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors collected particulate matter using high volume air samplers fitted with glass fiber filters. About 1000 m³ samples were taken and the filters Soxhlet extracted first with benzene and then with methanol. The extracts were reduced in volume and separated into acidic, basic, and neutral fractions. Conventional packed column GC/MS was used to identify and quantify the compounds. Nearly 60 neutral fraction hydrocarbons (alkanes, polynuclear aromatic hydrocarbons, and phthalate esters), 27 acidic fraction compounds (organic acids), and about 30 basic fraction compounds (organic bases) were identified. Many of the compounds were quantified as well. The authors also warned that losses of trapped organic compounds may be occurring during sampling due to evaporation (sublimation?). Two parallel samplers, operating for similar times but with different flow rates, produced nearly identical results when analyzed for organic content.

TITLE: A Fast Gas Chromatographic Method for Measuring C₂-C₆ Alkanes and Alkenes in Air

AUTHORS: Robert A. Cudney, Eric G. Walther, and William C. Malm

PERFORMING ORGANIZATION: Not specified

SPONSORING ORGANIZATION: Journal of the Air Pollution Control Association
27, 468-470 (1977)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors describe a dual column system that is tailored to capture and separate only the lighter hydrocarbons from an air sample. The first column, a 4 x 18" chromosorb 102 column is linked through suitable valving in the second column, a 16 x 1/8" 10% NaI on alumina column. Both columns are mounted in an oven that has cryogenic capabilities. The sample is pulled through column 1, which is maintained at -50°C. The system is then heated and the sample is eluted through both columns. Column 1 separates by increasing chain length, while column 2 separates alkanes from alkenes. The authors reported that the combination of both columns separated all hydrocarbon gases up to the hexenes, with the exception of the acetylene and isobutane pair.

TITLE: New Method for Calibration of Permeation Wafer and Diffusion Devices

AUTHORS: Russell N. Dietz, Edgar A. Cote, and James D. Smith

PERFORMING ORGANIZATION: Department of Applied Science, Brookhaven National Laboratory, Associated Universities, Inc., Upton, N.Y. 11973

SPONSORING ORGANIZATION: U.S. Atomic Energy Commission and U.S. Environmental Protection Agency

REPORT NO./JOURNAL: Analytical Chemistry, 46(2), 315-318 (1974)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors describe a pressure differential method employing a quartz, Bourdon pressure gauge. The system may also be used with noncondensable gases by hooking it up directly to a lecture bottle of the gas. As little as 6×10^{-7} gm of permeated gas can be detected by the system.

TITLE: Characterization of Sorbent Resins for Use in Environmental Sampling

AUTHORS: R. F. Gallant, J.W. King, P.L. Levins, and J.F. Piecewicz

PERFORMING ORGANIZATION: Aurthur D. Little, Inc., Cambridge, MA

SPONSORING ORGANIZATION: USEPA Office of Research and Development,
Research Triangle Park, N.C. 27711

REPORT NO./JOURNAL: EPA-600/7-78-054

NTIS/GPO NO.: PB 284 347

TYPE OF REPORT: Government Technical
Report

A comparison is made between two common resins XAD-2 and Tenax-GC for the collection of a wide variety of organic chemicals from air. Represented in the sampling are all of the common types of organic chemicals, including acids, alcohols, amines, aromatic hydrocarbons and aliphatic hydrocarbons. A method for estimating breakthrough volumes for individual organic chemicals is presented.

TITLE: Gas-Liquid Chromatographic -- Mass Spectrometric Investigation of C₆-C₂₀ Organic Compounds in an Urban Atmosphere

AUTHORS: K. Grob and G. Grob

PERFORMING ORGANIZATION: C-Labor der Universitat, Zurich, Switzerland

SPONSORING ORGANIZATION: F.J. Burrus et Cie., Boncourt, Switzerland

REPORT NO./JOURNAL: J. Chromatography, 62, 1-13 (1973)

NTIS/GPO NO.: N/A

TYPE OF REPORT: Journal Article

The authors collected pollutants from Zurich air on two, 25 mg, in-line charcoal filters. A 25-m³ sample was used for organics >C₁₂ and 250.l, for samples of hydrocarbons from C₆ to C₁₂. Desorption of the sample was accomplished by continuous extraction with 0.75 mL of CS₂. Identification required the use of capillary column gas chromatography/mass spectrometry (GC/MS). A special system that did not split the sample between the GC detector and the MS ion source was devised. The total sample was delivered to the input to the MS, greatly increasing the sensitivity of the method. One hundred eight compounds were identified in one air sample, mostly alkyl or aromatic hydrocarbons and a few oxygenated organic compounds.

TITLE: EPA/IERL - RTP Procedures for Level 2 Sampling and Analysis of Organic Materials

AUTHORS: J.C. Harris, M.J. Hayes, P.L. Levins, and D.B. Lindsay

PERFORMING ORGANIZATION: Arthur D. Little, Inc., Acorn Park,
Cambridge, Mass. 02140

SPONSORING ORGANIZATION: EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

REPORT NO./JOURNAL: EPA-600/7-79-033

NTIS/GPO NO.: PB 293800

TYPE OF REPORT: Government Technical
Report

This manual gives methods for the collection and analysis of environmental samples of industrial effluents.

TITLE: The Determination of Polynuclear Aromatic Hydrocarbons by Gas-Liquid Chromatography

AUTHORS: E.K. Harrison and C.I.B. Powell

PERFORMING ORGANIZATION: National Smokeless Fuels Ltd., Harrow,
Middlesex

SPONSORING ORGANIZATION: European Coal and Steel Community

REPORT NO./JOURNAL: Annals of Occupational Hygiene, 18, 199-206 (1975)

NTIS/GPO NO.: N/A

TYPE OF REPORT: Journal Article

A method for determining the polynuclear aromatic hydrocarbon composition of particulates from a high-volume air sample is presented. The sample was separated on polymetaphenoxylene and detected by both flame ionization and electron capture detectors. The difference in response by these two detectors towards pairs of unresolvable compounds allows for estimations of the composition of these pairs. Examples of separations are shown and were confirmed by fraction collection and thin layer and column chromatography followed by UV/visible spectroscopy.

TITLE: Extraction of Organic Compounds from Airborne Particulate Matter
for Gas Chromatographic Analysis

AUTHORS: H.H. Hill, Jr., K.W. Chan, and F.W. Karasek

PERFORMING ORGANIZATION: Guelph-Waterloo Centre for Graduate Work in
Chemistry, Department of Chemistry, University of
Waterloo, Ontario N2L 3G1 (Canada)

SPONSORING ORGANIZATION: Ontario Ministry of the Environment

REPORT NO./JOURNAL: J. Chromatography, 131, 245-252 (1973)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors compared the merits of using methanol vs. cyclohexane for the extraction of glass fiber filters for particulate collection from air. Glass fiber filters from a high-volume air sampler were divided into two equal parts and Soxhlet extracted with either 200 mL cyclohexane or methanol. The samples were reduced in volume, centrifuged to remove inorganic precipitates if necessary, and further reduced in volume to 1 mL. Identification and comparisons were made using conventional packed column GC. The methanol to cyclohexane extraction ratio was 1.69:1. Inorganic precipitates formed during the reduction of methanol volume and removed by centrifugation did not interfere with the method. Methanol extracts larger amounts and larger numbers of organic compounds from the filters.

TITLE: Enriching Volatile Compounds by a Temperature Gradient Tube

AUTHORS: R.E. Kaiser

PERFORMING ORGANIZATION: Institute of Chromatography, D-6702 Bad
Duerkheim, West Germany

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Analytical Chemistry, 45(6), 965-968 (1973)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The author describes a solid adsorbent, doubled-walled trap surrounded by a heating/cooling jacket. The device was assembled with several different adsorbents--molecular sieves B and C, Tenax GC, Dexsil GC 300 on Chromosorb W, and DC200 on Chromosorb. For collecting (enriching) the trap is cooled with an N₂ gas stream that has passed through liquid N₂. Thus the air inlet to the trap is maintained at -20°C and the air outlet is maintained at -160°C, causing trapping and partial separation of the organics in the incoming air sample. During desorption heated air is pumped into the end of the jacket nearest the incoming sample end (reverse direction to cool N₂ flow), maintaining the air inlet at +400°C and air outlet at +250°C. The sampler is useful for analyzing for C₁-C₄ hydrocarbons, a range usually lost during sampling using adsorbent methods.

TITLE: Potentially Hazardous Emissions from the Extraction and Processing of Coal and Oil

AUTHORS: H. Lebowitz, S. Tam, G. Smithson, H. Nack, J. Oxley, G. Cavanaugh, C. Burklin, and J. Dickerman

PERFORMING ORGANIZATION: Battelle Columbus Laboratories, Columbus, OH

SPONSORING ORGANIZATION: U.S. Environmental Protection Agency, Research Triangle Park, N.C.

REPORT NO./JOURNAL: EPA-650/2-75-038

NTIS/GPO NO.: PB 241 803 TYPE OF REPORT: Government Technical Report

This report presents flow diagrams for oil refining and coal conversion processes. The possible sources and potential toxicity of pollutants produced by these processes are listed. The study includes oil refining, coking, Lurgi high-Btu gasification, and solvent refining of coal.

TITLE: Talanta Review: Detection and Measurement of Volatile Hydrocarbons at Ambient Concentrations in the Atmosphere

AUTHORS: P. Leinster, R. Perry, and R.J. Young

PERFORMING ORGANIZATION: Public Health Engineering Laboratory, Imperial College of Science and Technology, London, SW7

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Talanta, 24, 205-213 (1977)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Publication, Review

This article is a general review covering all phases of sampling and analysis for volatile hydrocarbons in air samples for the period 1970-1976. The second on sampling includes both cryogenic and adsorptive sampling. References to all of the traditional methods for identification and quantification are included, among them gas chromatography, mass spectrometry, and spectroscopic methods. Listed in the bibliography are 125 references.

TITLE: Organic Characterization of Aerosols and Vapor Phase Compounds
in Urban Atmospheres

AUTHORS: G.D. Mendenhall, P.W. Jones, P.E. Strup, and W.E. Margard

PERFORMING ORGANIZATION: Battelle Columbus Laboratories, Ohio

SPONSORING ORGANIZATION: Environmental Sciences Research Lab,
Research Triangle Park, N.C.

REPORT NO./JOURNAL: EPA 600/3-78-031

NTIS/GPO NO.: PB 280 050

TYPE OF REPORT: Government Technical
Report

Both particulate and vapor samples were collected from urban areas of Missouri, Texas, Michigan, Colorado, and Florida. Particulate samples were obtained on a high volume sampler using a quartz fiber filter. Chromasorb 102 traps were used to collect vapor samples. Comparisons were made between filter extractions using Soxhlet extraction with benzene, methylene, chloride, and diethyl ether. The latter solvent was found to be unsatisfactory. The use of ultrasonic agitation with a suitable solvent was also attempted but resulted in high blank values. Chromosorb resins were thermally desorbed into a pre-GC trap. Particulate organic samples were subjected to elemental and infrared analyses. GC/MS analysis was carried out on the desorbed vapor phase organics. Up to 20 compounds or classes of compounds were identified in each sample.

TITLE: Determination of Trace Organics in Air and Water

AUTHORS: J.P. Mieure and M.W. Dietrich

PERFORMING ORGANIZATION: Monsanto Company, St. Louis, MO

SPONSORING ORGANIZATION: Monsanto Company, St. Louis, MO

REPORT NO./JOURNAL: J. of Chromatographic Science; 11, 559-570

NTIS/GPO NO.: N/A

TYPE OF REPORT: Journal Article

The authors describe a system for trapping trace organics on a short GC column. The column is filled with Chromosorb 101, Chromosorb 105 or Tenax GC and connected to an ordinary vacuum pump. The air sample is drawn through the column until a sufficient volume has been sampled. The short column is then returned to the laboratory, inserted into a GC oven and thermally desorbed into the inlet of a cool analytical GC column. The authors report that a 10-minute collection time is sufficient to allow detection of contaminants present at 1 ppb. The same system may be adapted for collection of trace organics in water samples.

TITLE: NIOSH Manual of Analytical Methods

AUTHORS: David G. Taylor (Manual Coordinator)

PERFORMING ORGANIZATION: N/A

SPONSORING ORGANIZATION: HEW, National Institute for Occupational Safety and Health, Cincinnati, OH

REPORT NO./JOURNAL: Vol I 77-157A
Vol II 77-157B
Vol III 77-157C
Vol IV 78-175

NTIS/GPO NO.: 77-157 A, B, and C TYPE OF REPORT: Government Technical
and 78-175 Report

The NIOSH manuals contain directions for sampling and analysis of several hundred chemical agents that may represent a hazard to a worker's health.

TITLE: Measurement of Carcinogenic Vapors in Ambient Atmospheres

AUTHORS: Edo D. Pellizzari

PERFORMING ORGANIZATION: Research Triangle Institute, Research Triangle Park, N.C.

SPONSORING ORGANIZATION: U.S. Environmental Protection Agency, Research Triangle Park, N.C.

REPORT NO./JOURNAL: EPA 600/7-78-062

NTIS/GPO NO.: PB 283 023 TYPE OF REPORT: Government Technical
Paper

In this report, the author further explores the use of Tenax GC for collecting trace organics from air. The results of samplings in various locations in the U.S. are presented. The use of permeation tubes for preparing vapor standards is extended to include some simple chlorinated hydrocarbons or aromatic hydrocarbons that are liquids at normal room temperature. The possible conversion of amines to nitrosoamines on Tenax GC was investigated. No significant amount of N-nitrosodimethylamine is formed when Tenax GC is exposed to a mixture of O₃, NO₂, NO, water vapor, and dimethylamine.

TITLE: Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres. The Performance of a Tenax GC Cartridge Sampler for Hazardous Vapors

AUTHORS: E.D. Pellizzari, J.E. Bunch, R.E. Berkley, and J. McRae

PERFORMING ORGANIZATION: Chemistry and Life Sciences Division, Research Triangle Institute, Research Triangle Park, North Carolina 27709

SPONSORING ORGANIZATION: U.S. EPA

REPORT NO./JOURNAL: Analytical Letters, 9(1), 45-63 (1976)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors compared the trapping efficiency of Tenax GC and Chromosorb 104 for a number of carcinogenic, volatile organic compounds. Variables that were investigated included breakthrough volume, the effect of different humidities on breakthrough volumes, repeated reuse of a resin, and the effect of storage and transportation on recoveries of the carcinogens. Tenax GC was determined to be a better adsorbent than Chromosorb 104 and was unaffected by different humidities or repeated reuse. Transportation and storage for 1 week did not affect recoveries if the samples were properly packed.

TITLE: Determination of Trace Hazardous Organic Vapor Pollutants in Ambient Atmospheres by Gas Chromatography/Mass Spectrometry/Computer

AUTHORS: E.D. Pellizzari, J.E. Bunch, R.E. Berkley, and J. McRae

PERFORMING ORGANIZATION: Chemistry and Life Sciences Division, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, N.C. 27709

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Analytical Chemistry, 48(6), 803-806 (1976)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

Vapor-phase organic samples were collected from urban air over Texas, North Carolina, and Florida. Tenax GC sampling tubes were used to concentrate the sample. More than 100 compounds were identified by using gas chromatography/mass spectrometry from a single air sample collected over Glendora, CA. Some comparisons between the contents of air at different locations were made.

TITLE: A Time-Based Elution Technique for the Estimation of Specific Hydrocarbons in Air

AUTHORS: R. Perry and J.D. Twibell

PERFORMING ORGANIZATION: Public Health Engineering Section, Imperial College, London

SPONSORING ORGANIZATION: Transport and Road Research Laboratory, Great Britain

REPORT NO./JOURNAL: Atmospheric Environment, 7, 929-937 (1973)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors sampled street air for vapor phase organic compounds by collecting the organic in a 25-L air sample on Chromosorb 102. The sample was then desorbed from the resin into the GC inlet. Instead of desorbing the whole sample, a carefully timed 5-sec elution was used. The amount of sample entering the GC inlet port is proportional to the total concentration on the resin. Standards are prepared and run in a similar manner. The utility of this system is to allow a small slug of carrier gas and sample to enter the GC, rather than to use the extended 10-min to 20-min desorption required by other methods.

TITLE: Equilibrium Vapour Concentrations of Some Polycyclic Aromatic Hydrocarbons, As₄O₆ and SeO₂ and the Collection Efficiencies of These Air Pollutants

AUTHORS: Christian Pupp, Robert C. Lao, John J. Murray, and Roswell F. Pottie

PERFORMING ORGANIZATION: Division of Chemistry, National Council of Canada, Ottawa, Canada K1A 0R9

SPONSORING ORGANIZATION: National Research Council of Canada

REPORT NO./JOURNAL: Atmospheric Environment, 8, 915-925 (1974)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

Equilibrium vapor pressure values (EVP) for some polynuclear aromatic hydrocarbons (PAH) commonly associated with polluted air were determined. The results were used to estimate losses due to sublimation of PAHs from high-volume air sampler filters during sample collection. Since the actual concentration of PAHs in air rarely exceeds the EVP, losses could be significant. The actual amounts lost would be determined by two factors, the extent of PAH adsorption on particulate or filter particles and the kinetics of sublimation. The effect of these factors would be to decrease losses from the maximum amount calculated on the basis of the EVP.

TITLE: Analysis of Air Pollutants Using Sampling Tubes and Gas Chromatography

AUTHORS: John W. Russell

PERFORMING ORGANIZATION: Analytical Laboratories, Dow Chemical Co.,
Midland, Mich. 48640

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Environmental Science and Technology, 9(13),
1175-1178 (1975)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors determined breakthrough volumes for 15 aromatic and phenolic compounds on Tenax GC. Poropak N was tested for 13 compounds, representing a wide variety of oxygenated, halogenated, and -CN compounds. Carbosieve B, Poropak R, and 20% DC-200 on gas chromatographic support were also tested. Tenax GC was determined to be the best overall adsorber, although the other resins may be useful for special cases. All supports were tested in a thermal desorption system connected directly to a packed-column gas chromatograph.

TITLE: The Sampling and Determination of Halocarbons in Ambient Air Using Concentration on Porous Polymer

AUTHORS: J.W. Russel and L.A. Shadoff

PERFORMING ORGANIZATION: Analytical Laboratories, Dow Chemical U.S.A.,
Midland, Michigan

SPONSORING ORGANIZATION: Not specified

REPORT NO./JOURNAL: Journal of Chromatography, 134, 375-384 (1977)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

Sampling tubes containing Poropak N porous polymer were used to sample halogenated hydrocarbons in air at Midland, Michigan, at parts per trillion levels. The samples were thermally desorbed into a cryogenic (-40°C) gas chromatography column and temperature programmed for analysis by GC with an electron capture detector. Confirmatory analyses were performed by using GC/MS to positively identify the halocarbons recovered from the air. Six different inorganic drying agents were tested to prevent the transfer of water from the Poropak N to the GC column during the desorption step.

TITLE: Performance of Permeation Tubes as Standard Gas Sources

AUTHORS: Bernard E. Saltzman, William R. Burg, and
Gopalakrishnan Ramaswamy

PERFORMING ORGANIZATION: Dept. of Environmental Health, University of
Cincinnati, Cincinnati, Ohio 45219

SPONSORING ORGANIZATION: Center for the Study of the Human Environment
U.S. Public Health Service and National Air
Pollution Control Administration

REPORT NO./JOURNAL: Environmental Science and Technology, 5(11),
1121-1128 (1971)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors describe a system for producing long lived (up to 1 year) permeation tubes. These tubes, which yield a reproducible controlled release of gas for the preparation of standard gas samples, are useful for preparing standards for easily liquefiable organic and inorganic gases. The principal disadvantage in earlier attempts to use permeation tubes was the short life of a tube after a long and tedious calibration procedure. The apparatus consists of a teflon permeation tube attached to a glass or stainless steel reservoir. The gas diffuses through the closed teflon tube at a controlled rate determined by the temperature of the system.

TITLE: Preparation of Known Concentrations of Gases and Vapors with
Permeation Devices Calibrated Gravimetrically

AUTHORS: Frank P. Scaringelli, Andrew E. O'Keeffe, Ethan Rosenberg,
and John P. Bell

PERFORMING ORGANIZATION: Division of Chemistry and Physics, National
Air Pollution Control Administration, Cincinnati,
Ohio 45226

SPONSORING ORGANIZATION: Division of Chemistry and Physics, National
Air Pollution Control Administration, Cincinnati,
Ohio 45226

REPORT NO./JOURNAL: Analytical Chemistry, 42(8), 871-876 (1970)

NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

This article describes the preparation of calibration of Teflon tubes for use as permeation tubes.

TITLE: Field Air Sampling of Pesticide Vapors with Polyurethane Foam
AUTHORS: Benjamin C. Turner and Dwight E. Glotfelty
PERFORMING ORGANIZATION: Agricultural Chemicals Management Laboratory,
AEQI, Agricultural Research Service, U.S. Dept.
of Agriculture, Beltsville, Md. 20705
SPONSORING ORGANIZATION: Not specified
REPORT NO./JOURNAL: Analytical Chemistry, 49(1), 7-10 (1977)
NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The ability of porous polyurethane foam to effectively trap vapors of 6 common pesticides was demonstrated. At a flow rate of 3.5 m³/hr, better than 99% recovery was achieved for dieldrin, heptachlor, trans-chlordane, lindane, trifluralin, and dacthal. The adsorbed pesticides were removed by Soxhlet extraction using hexane or benzene and analyzed by gas chromatography. Results for air sampling following field application of pesticides are given.

TITLE: Gas Chromatographic Analyses of Ambient Air for Light Hydrocarbons Using a Chemically Bonded Stationary Phase
AUTHORS: H.H. Westberg, R.A. Rasmussen, and M. Holdren
PERFORMING ORGANIZATION: Air Pollution Research, Engineering Research Division, Washington State University, Pullman, Wash. 99163
SPONSORING ORGANIZATION: U.S. Environmental Protection Agency
REPORT NO./JOURNAL: Analytical Chemistry, 46(12), 1852-1854 (1974)
NTIS/GPO NO.: N/A TYPE OF REPORT: Journal Article

The authors describe a procedure for identifying and quantifying C₂-C₅ hydrocarbons by gas chromatographic analysis on a chemically bonded stationary phase (n-octane/porasil C). The sample to be analyzed is trapped in a cryogenic tube after being dried over anhydrous K₂CO₃. The trap is then warmed and the sample is admitted to the inlet of a cooled (-70°C) Porasil column. A standard temperature programmed GC run is used to separate, identify, and quantify the compounds.

TITLE: Carcinogens Relating to Coal-Conversion Processes

AUTHORS: N/A

PERFORMING ORGANIZATION: TRW Energy Systems

SPONSORING ORGANIZATION: Fossil Energy Division, Energy Research and
Administration Development

REPORT NO./JOURNAL: FE-2213-1, June 14, 1976

NTIS/GPO NO.: Not stated TYPE OF REPORT: U.S. Government Technical
Report

This report lists the many organic chemicals formed during coal conversion that are carcinogens or suspected carcinogens. It provides descriptions of the different coal-conversion processes and tells what part of each process is likely to release carcinogens into the environment. A description of health-related research relating to coal conversion is included. One appendix, Epidemiological and Laboratory Studies Related to the Carcinogenic Properties of Coal-Carbonization Products, is included in the report.

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