CONSIDERATIONS FOR DESIGN OF SOURCE APPORTIONMENT STUDIES

A Report from the
Mathematical and Empirical Receptor Models Workshop (Quail Roost II)

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This report recommends procedures for source and ambient sampling and analysis in source apportionment studies. The recommendations are based on the results of receptor model studies of atmospheric particles in urban areas, especially a recent study of Houston, TX, undertaken as part of the Mathematical and Empirical Receptor Models Workshop (Quail Roost II). The recommendations are presented at three levels of increasing cost and detail of information obtained. Existing mass emissions inventories combined with chemically resolved test data from similar sources (not necessarily in the same locale) can be used to initially estimate the sources of elements present on ambient particles. To aid local users in construction of chemically resolved emission estimates, the U.S. Environmental Protection Agency (EPA) is compiling a library of compositions and size distributions of particulate emissions from major source types. More reliable source characterization can be achieved if the actual sources are tested directly. EPA should develop and publish detailed procedures for source sampling that would be more appropriate for receptor model use than are existing standard methods. Source and ambient sampling should be conducted by similar methods. If possible, particles from sources should be collected in a way that simulates changes that would normally occur before they reach distant receptors (e.g., by diluting and cooling the particles
It is recommended that particulate samples be routinely collected in two size fractions by use of virtual impactors, and that all samples be subjected, at a minimum, to mass and X-ray fluorescence analyses. Additional measurements are suggested for obtaining more detailed information: neutron activation analysis; X-ray diffraction; automated particle classification by electron microscopy; analyses for classes of organic species, $^{14}$C, and thermally released carbonaceous species; and real-time observation of several gases during sample collection. Methods for collecting meteorological data in parallel with ambient samples are described, as are methods for incorporating such data into the source identification process.

INTRODUCTION

This paper is the last in a series on the use of multi-species analyses of urban atmospheric particulate material and treatment of the results by receptor models in order to identify sources of the particles and estimate their contributions to ambient particulate levels. The entire series resulted from discussions and comparisons of analytical and interpretive methods conducted at the Mathematical and Empirical Receptor Models Workshop (Quail Roost II) (Stevens and Pace, 1984). In part, the Quail Roost II exercises involved application of various receptor models to ambient aerosol data obtained in Houston, TX. Johnson et al. (1984) describe the collection and analysis of particles from the Houston atmosphere, and Dzubay et al. (1984) examine the receptor model results obtained for that data set.
This paper sets forth recommendations for the design of receptor model studies of other urban areas. These recommendations are based on the results of the Quail Roost II study and of previous studies in other urban areas. We discuss improvements needed for future tests of receptor models and for application of receptor models to practical problems. As resources needed for an ideal study are rarely available, we suggest various types of source and ambient measurements that are appropriate at different resource levels.

The types of source measurements discussed include direct measurements at the source in question, the resolution of source terms from ambient sampling data by target transformation factor analysis, and a wind trajectory analysis method for identifying samples from ambient networks that are heavily influenced by specific sources. The discussion of ambient sampling covers not only the types of filters, samplers, etc., to be used, but also the need for adequate meteorological data and the methods needed for individual compounds in the particulate and gas phases.

SOURCE CHARACTERIZATION

**Direct measurements**

To identify and catalog source signatures, one must consider the following parameters: the number of sources present; the time (calendar dates) when tests and analyses were performed; the presence of unique pollutant emitters;
the variability in emissions composition of each source type; and the similarity of compositions of emissions from different types of sources. From these and other concerns peculiar to each site, a hierarchy of decisions must be made based on the questions to be answered and the resources available for the study. For example, if only compliance with a mass concentration standard must be determined, only the source types that contribute the majority of ambient mass may need to be assayed. However, if contributions to the concentration of a specific chemical species are needed, more detailed source signatures are required.

Resources are an important consideration in developing a receptor modeling program for any airshed. The following outline of three resource levels can be used to achieve various degrees of sophistication in a receptor model application. Each level depends upon completion of the previous level. Each level requires more resources than the preceding one, but provides receptor model results of greater reliability. An initial application of the receptor model using source composition data in each level may direct the actions and minimize the costs in subsequent levels. Obviously, we cannot give a single protocol that will be applicable to all locations and meteorological conditions, so the investigator must use judgment in deciding if some changes are needed for a particular study.

**Level I. Minimal resources.** The first step towards source characterization is to compile a list of the point and area sources most likely to affect pollutant concentrations at the sampling sites. Properties of their emissions can be estimated from available emissions inventories, site surveys, local
knowledge, and the results of previous tests of similar types of sources, not necessarily in the same locale.

For point sources, the National Emissions Data System (NEDS) and the local agency emissions inventories, from which NEDS is derived, are the best starting points. For each source emitting >1 t/yr of SO$_2$, NO$_x$, CO, or total emitted particulate matter (TEP), the NEDS condensed point source inventories contain source classification codes (SCCs) that identify the fuels used and processes involved, universal transverse Mercator (UTM) coordinates of the point of emissions, and calculated and allowable emission rates of SO$_2$, NO$_x$, CO, TEP, and hydrocarbons. These records are obtainable in computer-compatible formats that can be sorted by SCC and, subsequently, by TEP emission rates within each SCC. Important point sources of a given type should be identified on the basis of SCC and estimated TEP emission rate. The lower cutoff of emission rates will depend on the resources available. Past experience shows that most inventoried sources with TEP rates of <50 t/yr can be ignored unless they release fugitive emissions with low plume rise. The TEP rate is often inaccurate and should be treated as an order-of-magnitude estimate.

Individual sources and receptor locations should be plotted by UTM coordinates on a map of the area. If the intent is to determine contributions from individual sources, this map can be used to place receptors strategically. With knowledge of prevailing wind directions, one can place receptors so as to maximize the probability of collecting particles from the sources of major interest (see Wind Trajectory Analysis).
Area sources most likely to contribute to a receptor are those in its immediate environs. These sources are best identified from a survey of the area around the site. This survey, based on the National Air Monitoring System hardcopy site survey, should include:

1. A street-and-block map for the 2-km radius around the sampling site that shows typical traffic counts, curbing, lights, and general dirtiness of roadway sections; block classifications by residential, commercial, industrial, and agricultural categories; and locations and dimensions of vacant lots (with coverings), storage piles, and parking lots.

2. A description of the sampling station, including the sampler layout; elevation of sampling probes above sea level, ground level, and platform level; UTM coordinates; and a summary of nearby structures that might affect micrometeorology.

3. Photographs in eight cardinal directions from the sampling platform.

The point source summaries and site surveys should be reviewed by a knowledgeable person from the area. Local air pollution specialists are aware that emission rates often change more rapidly than indicated in emissions inventories and dated site surveys.

Source compositions for chemical components and particle size fractions under conditions compatible with those prevailing at the receptor should be
compiled from existing data for the source types in the area. This compilation would be assisted by a documented source characterization library. In such a library, data for each source should include its type, specific identifier, and the time, place, and circumstances of the source test; the characteristics of source operation and control devices used during the test; the sampling methods used for each test; the chemical species and size ranges measured and the analytical methods used; and concentrations and uncertainties therein for designated chemical species by size range. Some of this information is compiled in the Fine Particle Emissions Information System (FPEIS) (Schrag and Johnson, 1978).

Within the U.S. Environmental Protection Agency (EPA), the Air Monitoring Techniques Branch of the Office of Air Quality Planning and Standards recently initiated compilation of a source composition library that should contain sufficient information to allow selection of the source signatures that are most similar to those in the local area. At present, no existing document or computer library contains all available data on source signatures; consequently, data must be assembled from the relevant literature. Such literature includes previous receptor model studies in which the components are listed (Kowalczyk et al., 1982; Watson, 1979; Cass and McRae, 1981; Alpert and Hopke, 1980, 1981), published articles of reports of source studies, and soil analyses from the area based on national compilations (Shacklette et al., 1971) or those of state geological surveys. As discussed below, however, the airborne soil probably has a composition different from that of bulk soil. It may be preferable to construct an approximate component for emissions from coal-fired plants rather than to determine the composition directly from studies on plants from
another area. Such a component could be compiled on the basis of the composition of coal consumed in the local area as modified by enrichment factors determined for elements between coal and emitted particles (Gordon et al., 1981).

Most local areas will have insufficient funds for detailed studies of motor vehicle emissions, but a reasonable estimate of their compositions can be made on the basis of studies by Pierson and Brachaczek (1983), Ondov et al. (1982), and older work reported in the literature. As the compositions and masses of particles from diesel engines are quite different from those of gasoline-burning engines, the amounts of the different types of vehicle traffic in the area should be estimated from traffic counts or fuel sales.

Initial receptor modeling using these Level I source characteristics and receptor measurements can guide the efforts of Level II source characterization by evaluation of their adequacy for the models being applied.

**Level II. Moderate resources.** The accuracy and precision of estimates of source contributions can be improved if actual compositions of local source emissions are determined (instead of using measurements of similar sources in other locations). This section outlines a general method to be followed.

First, identify source categories and specific emitters that previous modeling or past experience have shown to be potential contributors. Major sources of mass include wind-raised or vehicle-entrained dust from agricultural soils, roadways, and parking lots; active storage piles (i.e., piles where
materials are frequently added or removed); transfer processes, such as loading and unloading of vehicles; and sources such as power plants, smelters, steel plants, cement plants, and refuse incinerators.

Second, from each selected source obtain "grab" samples that will best represent the average composition. Here "grab" sampling means the collection of bulk material from a pollution control device or from piles of material that may produce fugitive emissions, or the simple in-stack collection of suspended particles. Sampling methods used at each source should consider temporal variations caused by the process schedule and fuel switching.

Third, try to isolate the portion of the bulk sample that is likely to remain airborne long enough to reach a receptor. Ordinarily, it is inappropriate to analyze a bulk sample. A convenient and necessary (but not always sufficient) procedure is to sample in a suspension chamber after drying the bulk sample and sieving it through a standard Tyler 400-mesh (36-μm) screen. The resuspended sample should be collected on a filter of high purity (cellulose, polycarbonate, or Teflon) with a loading appropriate for the material to be measured and the intended analytical method. For example, a quartz filter cannot be used if silicon is to be measured.

If possible, the same size intervals used for ambient sampling should be used for source sampling. If sources are to be controlled to meet federal standards, the size intervals may be established by those standards. If not, the best scientific judgement should be followed, using available and convenient sampling methods. One useful approach is to employ virtual impactors.
(dichotomous samplers) to collect source and ambient samples in two size intervals (<2.5 μm and 2.5 to 10 μm).

For grab sampling of in-stack suspended particles, a variation of EPA Method 5 (Rom, 1972) is used in which the filter of Method 5 is replaced by a particle-sizing device, such as a cascade impactor (Pilat et al., 1970) or in-stack virtual impactor (Houck et al., 1982). In classical source emissions tests, a pitot tube must be used to determine the velocity of stack gases at many points along two perpendicular diameters across the stack. Then the mass loading must be measured at several points. However, for receptor modeling, collecting samples at one point somewhat away from the inner wall is usually sufficient. A pitot tube is used to determine stack gas velocity at that point, and the pumping speed through the sampler is adjusted to ensure iso-kinetic sampling. Several examples of stack studies are described by Klein et al. (1975), Gladney et al. (1976), Greenberg et al. (1978a, b), and Ondov et al. (1979a, b).

In the discussion of Level III procedures below, we recommend that stacks be sampled by dilution methods. If one owns the equipment needed for dilution sampling, the incremental cost of dilution sampling versus the methods described above will usually be a small fraction of the cost of stack sampling; in such cases, dilution sampling is recommended.

Finally, the samples should be analyzed for species of interest. At this second level of resources, consideration should be given to additional analyses that could improve the overall results, even though these additional species
have not yet been measured at the receptors. Analyses should be considered that would provide data compatible with ambient data on the following additional source characteristics: (1) total mass; (2) total mass within the "fine" and "coarse" size fractions; (3) individual elements and ions, especially major contributors to total mass or tracers for major sources; (4) inorganic and organic compounds, again emphasizing tracers for major sources; (5) visual characteristics, using microscopy of various types; and (6) crystal structures as observed by X-ray diffraction (XRD). (Note that we discuss analytical procedures below in connection with ambient samples. As virtually unlimited quantities of grab sample are usually available, one can assume that any analytical procedure appropriate for ambient samples can also be used here.)

This second level provides source samples similar to those taken at receptors at approximately the same cost per sample. Sources of some types may not be amenable to grab sampling, or the grab sample may not be representative of the emissions that reach the receptor. More complex and costly procedures are required to characterize these sources. Sampling only in stacks and pollution control devices will miss fugitive emissions, which often contribute more suspended particulate matter, especially in the coarse fraction, than do ducted emissions.

**Level III. Maximum resources.** Level III testing should be confined to those sources for which it is absolutely necessary, such as major contributors that are not amenable to grab sampling. In all cases, time variations in composition and mass should be determined for each source studied. The three types of Level III tests are:
(1) Ground-based sampling of plumes. This sampling should be completed for a source whose ground-level contribution is greatest. This type of test is applicable to sources such as motor vehicle emissions and field burns. The collection devices should be the same as those used at receptor sites. A variation of this method applicable to point sources -- wind trajectory analysis -- is discussed below.

(2) Dilution stack sampling. This technique should be used for vented emission sources and have appropriate constraints for assuring the collection of condensable species (Heinsohn et al., 1980; Houck et al., 1982). Samples should be collected in size fractions similar to those collected at the receptor sites. Presently, 2.5- and 10-μm diameter size cuts appear appropriate for the anticipated particulate matter standard. In the case of high-temperature stacks, provision should be made for diluting stack gases to ambient temperature and relative humidity to allow condensation of moderately volatile species. Standardization of the dilution sampler also is necessary, especially to determine the sample size required for the receptor application. If dilution and cooling are not possible, it is desirable to collect moderately volatile species (e.g., Hg, As, Se, halogens, organics) in appropriate columns or traps downstream from filters (e.g., activated charcoal) in order to determine an upper limit
on the amount that might condense in the plume at ambient temperatures (Germani, 1980). As these methods are still under study and improvement, no "standard" procedure can be described yet.

(3) Motor vehicle emissions. Ideally, one should be able to determine separate contributions from three vehicle-related components: emissions from diesel engines, from leaded gasoline engines, and from nonleaded gasoline engines. However, except for Pb and Br from leaded gasoline, these components are not well distinguished in an urban mix on the basis of elements per se. As other particle characterization methods (e.g., organic analyses, microscopy, etc.) are improved, they should be used to determine better markers for these components. In such studies, it is essential that hot exhaust emissions be cooled and diluted as discussed above. Alternatively, total emissions from vehicles can be measured effectively by studies in traffic tunnels, but the data must be collected and interpreted carefully to eliminate traffic-entrained soil from the true vehicle components (Pierson and Brachaczek, 1983). If there is sufficient variation of the diesel/gasoline traffic, one can probably resolve these components; however, it is difficult to see how one could separate leaded and nonleaded gasoline emissions in this way. Even if one could get an accurate count of these vehicle classes, there would probably be too little hour-to-hour variation of the ratio to permit resolution of their emissions.
Airborne sampling of plumes. Aircraft sampling of plumes from major sources can often be done quite effectively. If a fixed-wing plane is used, it should have as slow a stall speed as possible to maximize time spent in plumes and to decrease corrections needed for the response times of instruments that detect the plume. The aircraft should have two or four engines to leave the area around the fuselage free of propeller wash and engine exhaust. Collection probes should be designed to ensure that samples are collected isokinetically at a specified air speed, and that the intake is in a region of laminar flow, unperturbed by the plane. It should be possible to shut off filters (e.g., when outside of the plume) and to change filters during the flight. Sampling aircraft are usually equipped with real-time detectors of species indicative of the plume (e.g., \( \text{SO}_2 \), \( \text{NO}_x \), condensation nuclei), and data-loggers and/or strip charts so as to relate amounts of particulate matter collected to other plume indicators. Response times of real-time instruments should be as short as feasible (1 to 10 s), to give sharp changes at plume boundaries. It is expensive to modify a plane for sampling (usually requiring additional electric power and vacuum), and difficult to obtain FAA approval of the changes. However, once the changes are completed, plume sampling can be done very efficiently: under favorable conditions, plumes from several plants together with appropriate backgrounds can be sampled per day. The samples obtained are more appropriate for
receptor model use than are stack samples, and no cooperation of personnel at the source is required. A major limitation of aircraft sampling has been that no sampling device can collect material isokinetically in a size-segregated mode at a sufficiently high rate to provide enough material for many of the analytical techniques after just a few plume traverses. Perhaps the high-volume virtual impactor being developed and tested by Solomon et al. (In Press) will be useful in this application. Another problem, especially for sources in the midst of heavily populated areas, is that FAA restrictions may make it impossible to sample the plume at optimal locations or altitudes. An example of aircraft plume sampling of several copper smelters is the work of Small et al. (1981). Tethered balloon sampling systems offer an alternative method for sampling plumes (Armstrong et al., 1981). Such systems allow rapid horizontal and vertical mobility for plume sampling and can be used to collect samples over longer time periods than are practical with planes.

Procedures required. If receptor models are to be widely used by state and local air pollution authorities, EPA needs to develop standard procedures for obtaining the data that are used in these models. In some cases, especially for Level III procedures, research will be needed before the procedures can be written.
Level I procedures should cover the following areas: (1) reducing NEDS Point Source Inventories for receptor model applications; (2) making surveys of areas around receptor model sampling sites; (3) using the Receptor Model Source-Composition Library; and (4) assembling source compositions from the Library that are appropriate to the local area. Level II procedures should provide guidance for: (1) obtaining representative grab samples from storage piles, baghouses, roadways, parking lots, and exposed land; (2) drying, sieving, and resuspending grab samples for specific analyses; and (3) taking size-segregated stack samples. Level III procedures should cover these areas: (1) ground-based sampling for source emissions characterization; (2) dilution sampling of stacks and ducts for source emissions characterization; and (3) airborne sampling of elevated plumes for emissions characterization.

Estimation of source signatures by multivariate methods

For the Quail Roost II workshop, a multivariate method, target transformation factor analysis (TTFA) (see Henry et al., 1984), was used to estimate source profiles from the ambient data. Once source profiles have been determined, ordinary chemical mass balance (CMB) methods may be used to determine source impacts. This procedure is valuable if the only available source profiles are from source tests conducted in other geographic areas, or if it is reasonably certain that the source profile has changed or is highly variable. TTFA can be used to adjust an assumed source profile to maximize that profile's consistency with observed intercorrelations. Thus, TTFA can improve the source profile before ordinary CMB analysis is attempted. If sufficient data are available (30 or more degrees of freedom per variable), TTFA can provide a
useful check on assumed source compositions. If no source composition data are available, TTFA can provide quantitative estimates of source profiles. For instance, if a previously unknown source is deduced, its approximate composition can be determined.

Certain dangers are associated with the use of TTFA to obtain source signatures, especially the "smearing" of signatures between sources whose emissions are highly correlated in time or space. Hopke and Gordon (unpublished results) have compared results from CMB (Kowalczyk et al., 1982) and TTFA for 130 samples from the Washington, DC area. Signatures obtained by TTFA for marine aerosol and incinerator emissions contained admixtures of the signature of oil-fired power plants (indicated by high V and Ni concentrations). This smearing of signatures, which resulted from correlations among those source emissions, reflects the close proximity of an oil-fired plant to an incinerator in Washington and the fact that large oil-fired plants are located to the south and east of Washington, so that air parcels coming from those directions, bearing marine aerosol, also contain particles from oil combustion. A comparison of signatures of sources in St. Louis obtained by TTFA (Alpert and Hopke, 1981) and wind trajectory analysis indicates a similar smearing of signatures by TTFA among sources that are located in the same general direction with respect to the receptor. In cases of large ambient data sets that include extensive meteorological data (especially wind direction), the smearing problem may be avoided by selectively applying TTFA to only the samples collected under specified wind conditions.
Gordon (1980) has reported on the use of wind trajectory analysis (WTA) for obtaining compositions of particles from specific sources by using large ambient data sets that contain extensive wind direction data -- in particular, the St. Louis Regional Air Pollution Study (RAPS) data set (Stevens et al., 1978; Loo et al., 1978; Dzubay, 1980). The method has been further developed by Rheingrover and Gordon.

In WTA, the following steps are performed for each species in each size fraction:

a. Determine average concentration and standard deviation at each station.

b. Search the data from each station for sampling periods that meet two conditions: a concentration of \(~3\sigma\) above average for the station; and fluctuations of surface wind direction, \(\sigma_\theta\), of less than \(~20^\circ\).

c. For sampling periods that meet these criteria, construct a histogram of mean wind direction. If there are dominant sources of the species, the histogram will display clusters about angles pointing toward the sources.
d. Using the mean angles from the clusters, construct a map of back trajectories observed at all stations in the network. A convergence of trajectories from two or more stations often indicates the presence of a dominant source of the species near the convergence.

e. For samples identified as heavily influenced by a particular source, construct linear regressions of concentrations of all measured species versus those of one or more species strongly associated with particles from the source. The correlation coefficients indicate the likelihood that the various species are present on particles from the source, and the regression coefficients yield relative concentrations. If mass contributions from the source are large enough to give good correlations with the species in question, absolute concentrations of those species in the particulate matter can be obtained.

Rheingrover and Gordon (1980) used WTA to identify samples influenced by the following point sources in St. Louis: an iron and steel complex, an iron works, a zinc smelter, two lead smelters, two copper plants, an incinerator, a pigment plant, and a fertilizer plant. Surprisingly, they also found trajectories -- apparently to areas of high traffic density -- that were associated with motor vehicles. For most sources, concentrations of 6 to 10 elements relative to that of a prominent element could be determined.

WTA has several advantages relative to traditional methods:
(1) It avoids the cost of source measurements.

(2) The source signatures obtained are characteristic of particles as received at the receptors. For example, volatile elements will have condensed (if they are going to), and very large particles will have fallen out.

(3) Problems that could arise by use of different sampling equipment or analytical methods at the source versus the receptors, or by use of measurements widely separated in time, are avoided.

(4) Fugitive emissions, which are difficult to measure by conventional methods, can often be observed.

(5) Cooperation of personnel at the source is not required.

The use of linear regressions to obtain the compositions of source particles presupposes that fluctuations about the regression lines are random. However, aside from experimental error, the fluctuations result from real variations of intensities of components from other sources. Consequently, one should be able to resolve the other components by a multivariate method to leave a more accurately known component for the source in question. Chang et al. (1982) have subjected the groups of St. Louis trajectory samples identified by WTA to TTFA to obtain more comprehensive, reliable composition patterns for the sources identified.
Another feature of WTA is just beginning to be exploited. X-ray fluorescence (XRF) is a rapid, inexpensive method for analyzing vast numbers of samples that can be used to provide data for WTA. The latter can identify the samples containing large contributions from specific sources. The samples so identified can be subjected to more elaborate studies that would be prohibitive to perform on the entire set. Two uses of XRF/WTA as a screening method are in progress. In the first, Gordon et al. (1982) obtained samples from the RAPS set that were identified by WTA as containing heavy loadings of particles from specific sources and analyzed them by instrumental neutron activation analysis (INAA) to obtain data for more elements than are observed by XRF. Second, Jaklevic (unpublished results) is subjecting some of the identified samples to XRD in an attempt to observe specific minerals. Many other sophisticated techniques (e.g., microscopic methods) could be applied to the identified samples.

The WTA method depends on the availability of a very large data set -- a minimum of several hundred samples collected for ≤12-h periods by each of three or more strategically located dichotomous samplers and analyzed by XRF. At least one recording wind vane should be included in the network. If Level II ambient sampling (see below) is done routinely, several months of data would be sufficient for application of WTA. In future sampling programs, receptors should be carefully placed with respect to sources and prevailing winds to maximize the potential for subsequent WTA. Appropriate wind data must also be obtained to define the influence of local versus regional sources.
No single protocol for sampling and analysis is applicable for all receptor model studies. Below we present an ideal hierarchy of sampling and analysis procedures of increasing sophistication and cost. However, if resources are limited, a decision must be made regarding the optimal division of those resources between source measurements, ambient sampling and analysis, meteorological measurements, and interpretations. The division of effort among these categories to achieve a given level of reliability of final results (e.g., accuracy of the estimates of total suspended particulate contributions in two size fractions from various source classes) will vary for different areas. If most important sources in an area are common to many areas (e.g., coal- and oil-fired power plants, motor vehicles, marine aerosol, soil, and regional sulfate), little additional study of sources may be needed. (However, the EPA 1980 Houston study demonstrated the need for at least some analyses of sieved, resuspended soil, whose composition may vary considerably from one area to another.) In these cases, most resources would be best devoted to ambient measurements. On the other hand, if an area contains sources that are unique or whose emissions are poorly described, considerable effort should be made to characterize those sources. For example, Houston has a number of industrial sources, especially in the petroleum and petrochemical industries, whose emissions are not well characterized. This fact, coupled with the unusual composition of Houston soil (e.g., its very large calcium concentration from marine shells), caused considerable confusion in the application of CMB interpretations. The final product would have been more reliable if more source information had been available.
Although ambient measurements are the focus of this section, ambient and source measurements should be considered together. Insofar as practical, similar collection and analysis methods should be used for both types of measurements (e.g., inlet cut point, type of sampler and filter media, analytical techniques).

**Sampling**

**Particle samplers.** In view of the availability and detailed characterization of the dichotomous sampler of the virtual impactor type, this device should be considered the basic sampler for receptor model applications and should be used at each sampling site. Particles of >2.5 µm in diameter are chemically quite different from those of <2.5 µm. These groups should be kept separate to avoid the loss of information that occurs if they are mixed. Cascade impactors can separate particles into six or more fractions, but the additional fractionation often does not add much useful information. Studies on power plants and other combustion sources indicate that particles of <0.2 µm in diameter constitute another qualitatively different group (Ondov et al., 1981), but as yet no collector is routinely available. This group might be useful for identifying sources if enough of the particles survive coagulation to be observed. If, as appears probable, EPA adopts a standard for particles of <10 µm in diameter, the upper cut point should probably be adjusted to that size. The 2.5-µm cut point, however, should be retained for identification purposes, whether or not a standard is established for the fine particles.
The filters routinely used in dichotomous samplers should have low blank values for elements of interest. Teflon and low blank Nuclepore filters meet this criterion for analyses by XRF. If it can be done without contaminating samples, the coarse-fraction filter should be coated with a substance that will prevent particle loss during handling. Either of the commercial samplers (Beckman and Sierra) with flow rates of 17 L min$^{-1}$ or the Berkeley sampler (Loo et al., 1978) with a flow rate of 50 L min$^{-1}$ will provide enough sample for XRF and nuclear analysis. Mass can be determined by β-gauge (Jaklevic et al., 1981; Courtney et al., 1982).

The measurement of particulate mass and elemental concentrations represents the minimum level of ambient sampling and analysis for receptor modeling. Preferably, several additional measurements should be performed: particulate ionic species, carbon, organic compounds, crystalline substances (by XRD), individual particles (by electron microscopy), and gases. The additional measurements require that other samplers be run in parallel with the main samplers (namely, dichotomous samplers with either quartz filters for carbon and ionic analyses or Nuclepore filters for microscopy). XRD measurements can be performed on samples acquired with ordinary dichotomous samplers using Teflon membrane filters. However, optimum detectabilities for minor components require loadings of >100 μg cm$^{-2}$. Most crystalline species can be measured with minimum detectabilities of better than 5 μg cm$^{-2}$ using the Berkeley diffraction system (Thompson et al., 1982). If costs are too high to permit the various samplers to be run concurrently, some savings are possible by collecting samples for microscopy -- which does not require high loadings -- for short periods in between collections for XRF, using the same samplers.
Sampling and analysis methods for organic compounds are still not as well developed as those for inorganic species, and there are no routine sample collection protocols. However, most analytical methods require large amounts of particulate material (i.e., 10's to 100's of milligrams). At present, the samples can be collected with a quartz hi-vol filter, although information on particle size will be sacrificed and the filters may adsorb some organic vapors. Size information could be obtained, if necessary, with and without a cyclone in front of the filter. Preferably, particles for organic analysis should be separated into two size groups, as the large-particle fraction may contain carbon in the form of bugs, pollen, carbonate, etc., whereas the compounds of interest for receptor modeling will be present mainly in the fine fraction. A developmental high-volume dichotomous sampler (~500 L min⁻¹) being tested by Solomon et al. (In Press) may be of great value for collecting large masses of material.

**Other samplers and instruments.** The value of the data will be greatly enhanced if they include information on pollutant gas concentrations, condensation nuclei concentrations (CNC), and the light scattering coefficient (b_{scat}). These quantities can be measured in real time with rather high reliability by use of commercial instruments (if carefully calibrated and frequently serviced). Flame photometric total sulfur analyzers mainly measure SO₂. Chemiluminescence detectors are available for O₃ and for NO and, in a separate mode, for NO plus species that can be reduced to NO (mainly NO₂). The best available instruments, with the possible exception of the NO/NOₓ detector, have sufficiently low detection limits to usually provide valid readings in an urban setting. Carbon monoxide can be measured accurately with infrared instruments. An
integrating nephelometer is commonly used to measure light scattering, as is a condensation nuclei counter for CNC. As these are real-time devices, their readings should be frequently recorded by a data-logging device whose record can be read by a computer so that appropriate averages and standard deviations can be calculated. Depending on the number of input channels of the data-logger, it may also be used to store meteorological data.

In addition to the standard pollutant gases (CO, SO_2, NO/NO_x, and O_3), many other gases and vapors, if measured, could provide information of value for receptor modeling. Among these species are a wide range of hydrocarbons and other organic compounds and volatile forms of such elements as Hg, Se, and the halogens. Methods for collection and measurement of some of these are reasonably well established (e.g., the collection of hydrocarbons in Teflon bags followed by analysis using gas chromatography, possibly coupled with mass spectrometry). Multiple columns in series have been used by Braman and Johnson (1974) to collect four different forms of airborne Hg, and Germani (1980) has used activated charcoal traps to collect volatile forms of several elements. However, despite the potential values of these types of measurements, we do not recommend their use in any but the most advanced, developmental receptor model field studies. Many of the collection and analysis methods are far from standard, and a more serious problem is that even if emission patterns are known, we know little about the modifications of these species during transit to the receptor. Modifications could result from reactions with species such as ·OH radicals, preferential condensation on airborne particles, or ground-level deposition.
A summary of a complete sampling station meeting all of the above needs is given in Table 1.

**Sampling locations and periods.** Most studies in urban areas will require at least six sampling stations (more if there are unique sources). All should be equipped with dichotomous samplers to permit subsequent XRF analyses, and at least one should be equipped with the samplers needed for the additional analyses discussed above and below. Before locations are picked, wind direction frequency distributions (wind "roses") should be used to place stations so that they will receive emissions from major sources under predominant wind conditions, and so that the sources can be discriminated from each other by wind trajectories at clearly different angles from certain stations.

Because of the large meteorological changes that often occur between night and day, sample collection times should be \(<12\) h in urban areas, and filters should be changed in the early morning and evening. If affordable, samples should be collected every 6 h, which greatly increases the probability of constant wind direction during sampling and, hence, the possibility for obtaining directional associations of collected particles. Reductions to less than 6 h are probably not cost-effective except to obtain the lightly loaded samples needed for microscopic studies, and even 6-h samples may not contain sufficient material for XRD.

**Meteorology.** A severe limitation of most previous studies has been the lack of adequate meteorological data. Hourly observations of instantaneous wind direction from the nearest airport are insufficient to determine the
directions of important sources with respect to samplers. At least one sampling location should be equipped with a meteorological tower to obtain wind direction and speed with sufficient frequency to calculate hourly average values and standard deviations. If feasible, especially in a large study area, more than one station should be so equipped.

To relate results to dispersion models, one needs information on mixing heights and stability class. Classical methods such as balloons and radiosondes are helpful, but usually too expensive to use more than twice a day. Devices that yield more frequent readings should be considered: for example, a meteorological tower for short-term wind fluctuations or vertical temperature gradients ($\Delta T/\Delta z$) to calculate stability class, or an acoustic sounder to obtain mixing height. As development and testing increase their reliability and reduce their costs, various remote sensing devices should be considered for these applications. For example, laser radar (Lidar) instruments measure particle light-scattering versus altitude from ground level, or temperature versus altitude via population of rotational states of molecules of $\text{H}_2\text{O}$, $\text{CO}_2$, etc. These devices may be costly, but they permit the investigator to make frequent observations of temperature gradients, mixing heights, etc., at a fraction of the operating costs of traditional methods.

**Analysis**

As with the source studies and sampling, here we present a hierarchy of measurements of increasing sophistication and cost. The choice of analytical measurements should be based on the resources available for the study, the
species to be measured, and the kinds of ambient samples collected. Obviously, the sampling methods are closely coupled with the analytical measurements; for example, certain analytical measurements cannot be performed unless the samples have been collected in a specific way.

Certain of the sample treatment and analytical methods discussed below remain under development. Some of the problems that require further research have been discussed in more detail by Hauser et al. (1983).

Particle analyses. The following criteria are considered in approximate order of increasing cost and information content.

Mass. At a minimum, the mass concentration in each size fraction should be measured. Historically, air filters were weighed under controlled humidity before and after particle collection. Mass concentrations for low-volume samples are now often measured by β-gauge, that is, by placing the filter and particle deposit between a radioactive β-emitting source and a detector and observing the reduction of count rate (Jaklevic et al., 1981; Courtney et al., 1982). This technique can be automated for measurement of large numbers of samples, and the results obtained for Teflon filters agree with those obtained by electrobalance (Courtney et al., 1982).

Elements. Most receptor model studies involve such a large number of samples that traditional chemical methods are impractical. Automated XRF methods have been developed that involve the sequential use of three secondary fluorescers to emphasize elements in various regions of atomic number. They are
capable of analyzing for up to 25 elements per sample over a few minutes (Stevens et al., 1978; Loo et al., 1978). Fig. 1 compares typical concentrations of elements in urban atmospheres with detection limits for XRF and INAA (Dzubay, 1977; Cooper, 1973). Table 2 lists the elements that were easily, marginally, or not observable in the St. Louis RAPS.

XRF is fast and inexpensive, but cannot be used to determine accurately elements lighter than Al, nor routinely to observe various minute trace elements such as Se, As, and Sb, which may yield more definitive signals of certain sources than more abundant elements. Thus, funds permitting, some samples should be analyzed using a different technique to extend the number of elements observed. A particularly useful combination is XRF followed by INAA. The latter technique is totally instrumental and, depending on mass loadings and filter blanks, can observe up to 40 elements (Kowalczyk et al., 1982). Gordon et al. (1982) demonstrated the value of applying INAA to samples from the RAPS that had previously been subjected to XRF. Table 2 is based on their results, which show that the combination of XRF and INAA yielded data for 29 elements in the fine fraction and 32 in the coarse fraction for virtually every sampling period. An additional 18 elements in the fine fraction and 14 in the coarse fraction were observable in about half of the samples. Furthermore, 11 elements (Al, Ca, K, Cl, Ti, V, Mn, Fe, Zn, Br, and Ba) can usually be measured by both methods to serve as a quality assurance check. Thorough INAA requires access to a reactor with a flux of at least $10^{13} \text{n cm}^{-2}\text{s}^{-1}$ and a high-resolution Ge(Li) or intrinsic Ge $\gamma$-ray spectrometry system. The well thermalized neutrons of heavy water moderated reactors avoid inter-element interferences among light elements caused by fast neutrons in light water reactors. However, the fast
neutrons allow one to observe Ni via an (n,p) reaction in light water reactors. Irradiations of two different lengths are needed for species of various half-lives (see below).

As presently performed, INAA requires considerably more sample handling and interpretation of results than XRF and, consequently, is considerably more costly per sample. Thus, XRF is the preferred screening technique. All samples could be subjected to XRF and the results used to identify only the most interesting samples for further analysis by INAA (for example, those heavily influenced by particles from certain major sources).

Another way to economize INAA is to use an approach taken by the Oregon Graduate Center (Watson, 1979; Core et al., 1981). Complete INAA requires at least two irradiations of samples, the first for a few minutes to observe species with half-lives of \( \leq 15 \) h, and the second for several hours to observe species with half-lives of up to several years. The former are much cheaper to perform, as the \( \gamma \)-ray spectra are simple enough to be resolved primarily by computer. Furthermore, in the former, results are usually available within a day after the irradiation, compared with about three weeks for long irradiations. The Oregon Graduate Center group has employed INAA cost-effectively by performing only the short irradiation following XRF analyses. Depending on the conditions, most of the following elements are usually observed: Na, Mg, Al, S, Cl, K, Ca, Ti, V, Mn, Cu, Br, La, Sm, Dy, and W. However, some important elements that are normally observed in long irradiations (Cr, Co, As, Se, and Sb) are usually sacrificed in this approach.
Many other techniques are used to observe elements in atmospheric particulate matter, including atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrometry (ICPS), spark-source mass spectrometry, various electrochemical methods (such as anodic stripping voltammetry), and chemical separations followed by colorimetry. Most require considerable labor per sample to obtain accurate results, or (unlike XRF and INAA) require dissolution of samples prior to analysis. Moreover, any chemical manipulation greatly increases the chance of contamination by trace elements and loss of volatile or insoluble species.

Ionic species. We should not only know the concentrations of a large number of elements, but also the ionic forms of certain major species: for example, \( \text{H}^+ \), \( \text{NO}_3^- \), \( \text{NH}_4^+ \), and \( \text{SO}_4^{2-} \). These species can be measured on Teflon filters from dichotomous samplers, as in the Houston study (Johnson et al., 1984; Dzubay et al., 1982). In that case, the samples were preserved immediately after sampling by placing them in an extraction solution of \( \text{NH}_4\text{Cl} \) and \( \text{HClO}_4 \) of known concentrations. Total acid was determined by Grans titration, and \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) were determined by ion chromatography (IC). Under favorable conditions, many anionic species can be determined by IC, including \( \text{NO}_2^- \), \( \text{NO}_3^- \), \( \text{SO}_3^{2-} \), \( \text{SO}_4^{2-} \), \( \text{Br}^- \), \( \text{Cl}^- \), \( \text{F}^- \), and \( \text{PO}_4^{3-} \), but the validity of \( \text{NO}_2^- \) and \( \text{SO}_3^{2-} \) is questionable because of possible instability of the oxidation states. Although \( \text{NO}_3^- \) can be measured accurately, there is considerable question about artifact formation (positive or negative) during collection. The filters recommended here, however, should have negligible artifacts for \( \text{SO}_4^{2-} \). In principle, a number of cationic species (\( \text{NH}_4^+ \), \( \text{Na}^+ \), \( \text{K}^+ \), etc.) are detectable by IC using a different column, but this is rarely done, except for \( \text{NH}_4^+ \). The last may be
observed by a colorimetric procedure (Rassum and Villarruz, 1963), as in the Houston study. Similarly, NO$_3^-$ can be observed by a colorimetric method (Jassens and Dams, 1974), and water-soluble SO$_4^{2-}$ can be assayed by placing a water extract of the filter in a filament and flash-vaporizing it into a total sulfur analyzer (Husar et al., 1975).

Carbon. Carbon may account for 10 to 30% of the particulate mass, of which perhaps two thirds occurs in the fine fraction. At a minimum, the total carbon should be measured, possibly by combustion and measurement of the CO$_2$ released. The carbon released as a function of temperature in differential thermal analysis also should be measured. Organic materials are released at fairly low temperatures and elemental carbon at much higher temperatures (Johnson et al., 1981). If the latter is coupled with measurement of light transmission through the filter versus temperature, additional data are provided on the absorption coefficient of particulate matter, $b_{ap}$, a factor that contributes appreciably to visibility degradation (about 6 to 13% in Houston) (Dzubay et al., 1982). In the past, the fraction of carbon extracted by organic solvents such as benzene was frequently measured. Grosjean (1975) showed, however, that this nonpolar solvent does not give complete recovery of particulate organic carbon, and recommended that a nonpolar and a polar solvent be used as a binary mixture or in sequence.

Converting carbon to CO$_2$ and then using a low-background $\beta$ proportional counter to measure the $^{14}$C-to-total-carbon ratio has been used to considerable advantage in a few studies (Cooper et al., 1981). This ratio indicates the fraction of particulate carbon arising from fossil fuels versus that from
"modern" carbon sources, such as the combustion of vegetation or recently living wood. Fossil fuels contain no $^{14}\text{C}$, whereas modern sources have a $^{14}\text{C}$-to-total-carbon ratio approximately equal to that of the atmosphere. In the Houston study, even using the very-low-background counter at the National Bureau of Standards, the sample mass requirements necessitated use of a quartz hi-vol filter behind an inlet consisting of six coaxial cylinders that removed most particles of $>4$ μm in diameter. Recently, considerable progress has been made in increasing the sensitivity of $^{14}\text{C}$ measurements by use of nuclear particle accelerators. With this method, samples containing <50 μg carbon (versus milligram quantities with counters) can be used, thus eliminating the need for special high-volume collections (Currie and Klouda, 1982). At present, few U.S. laboratories can perform the $^{14}\text{C}$ measurements.

Organic compounds. Although not used in the Houston study, one of the potentially most useful techniques for receptor model application is the analysis of particles (and, possibly, vapors) for organic compounds. Such a multitude of organic compounds is present in the atmosphere (Daisey, 1980; Daisey and Kneip, 1981; Simoneit and Mazurek, 1981) that measurement of many members of appropriate compound classes could provide very high resolution of sources, if certain conditions were met. The study of organic compounds is needed particularly for the identification and assay of particles from sources that release mostly carbonaceous particles that provide little or no signal via the elements observed by XRF and INAA (e.g., engines burning diesel fuel or unleaded gasoline, home heating, refineries, coke ovens, petrochemical plants). Perhaps because of the carcinogenic nature of many of its members, the series of polynuclear aromatic hydrocarbons (PAHs) probably has been the most
extensively studied (Daisey, 1980; Daisey et al., 1979; Hites, 1981; Hites et al., 1977; Fox and Staley, 1976). The PAHs do fulfill a major need of markers for receptor models in that relative intensities of the various members appear to differ depending on the type of source, the combustion temperature, etc. However, other classes of organics, especially the long-chain aliphatic compounds, contribute much greater masses of material (Daisey, 1980; Lamb et al., 1980; Simoneit and Mazurek, 1981). Thus, the study of organic compounds should include observations of several classes of compounds. Before organic compounds can be routinely used, the following investigations should be made:

a. Carefully review existing source emissions data to identify compound classes that may be of potential use in distinguishing source types. Then perform extensive studies on major sources of carbonaceous particles to determine the compound classes that show the greatest pattern differences between source types.

b. For those classes that appear promising, establish the fraction of each member that is typically in the gas phase, and determine how that fraction changes with distance from the source or variation of ambient conditions. For these studies, both filters and downstream polyurethane plugs should be analyzed (Yamasaki et al., 1982; Glotfelty et al., 1983). Tenax plugs have commonly been used for this purpose, but flow rates through them are so low that it is difficult to collect enough material for some analyses. If polyurethane is used, a series of columns should
first be used to ensure that the species of interest do not penetrate the column over the sampling duration.

c. Identify the organic compounds that, upon release, are stable or react slowly enough that transformation can be ignored.

Analytical methods for PAHs (e.g., GC and high-performance liquid chromatography) are well developed. A calibration standard (PAH in acetonitrile) and a particulate matter Standard Reference Material certified for certain PAH compounds have recently become available through the National Bureau of Standards (May et al., 1982). Capillary column GC/MS has proven to be a valuable analytical method for multi-compound analysis of nonpolar, volatile organic compounds in particulate matter. The accuracy of this method, however, is limited by the availability of standard compounds. Methods for more polar organic compounds and for labile compounds are not well developed.

Crystals. A prospective method to identify particle sources is to observe various crystalline materials according to their XRD patterns. Thompson et al. (1982) at Lawrence Berkeley Laboratory (LBL) have developed an XRD unit specifically for analysis of air filter samples. With it they are able to observe a number of minerals in particulate material, including quartz, calcite, dolomite, halite, mascagnite, and lead ammonium sulfate. The ability to observe minerals in the Houston study was limited by the particulate loading of the dichotomous sampler filters (typically 70 \( \mu \text{g} \text{ cm}^{-2} \)) and the fact that the LBL instrument was not yet fully operational. Particulate loadings of >200 \( \mu \text{g} \text{ cm}^{-2} \) are optimum for XRD, and the sensitivity of the LBL instrument has now been
improved to give detectabilities of <5 μg cm\(^{-2}\) for major crystalline species. If greater sensitivity is required, the XRD technique should be applied to samples collected with hi-vol filters with and without cyclones upstream.

Individual particle analysis. In the Houston study, Johnson et al. (1984) used computer-assisted scanning electron microscopy with automated image analysis and X-ray energy spectroscopy (SAX) to scan the filters and classify individual particles according to their shapes, sizes, and XRF analyses for several elements. Each particle was classified according to source type by comparing the measured parameters against those of 25 particle classes stored in a library. Most of the library classes were developed from previous studies in other areas, although Houston soils were observed and included. The coarse-fraction samples from Houston had loadings of 50 to 60 μg cm\(^{-2}\), which provided a particle spacing on the filters that was appropriate for observation. Particles could be sorted into about a dozen categories. Analyses of the fine-fraction samples were much less successful, because the much higher particle number density (especially of secondary sulfate particles, which coated most of the area) made it difficult to observe other types of particles.

This method is still highly experimental but holds great promise because of its high resolution, that is, its ability to sort particles into as many as 25 classes. In future receptor model studies, particulate samples from the major sources should be collected with loadings appropriate for SAX to build a library of characteristics of particles from sources in the area. In both source and ambient sampling, fine-fraction samples for SAX should be collected for shorter times than the coarse fractions, to obtain optimal spacing of particles on the filters.
Gases. Very thorough studies, such as the RAPS, have included measurement of several gases (e.g., SO₂, O₃, NO, NO₂, CO) simultaneously with particle collection. However, most receptor model treatments have focused on the composition of the particles and have largely ignored the gas data. But the gases also carry information about sources (e.g., CO from motor vehicles, SO₂ from power plants and smelters, NO from high-temperature processes and consequent deficiency of O₃ from reaction with NO). The gases should be measured at both sources and receptors, and the information used along with the other parameters in receptor model calculations. Gas measurements are real-time measurements with <1-min response times, so they can add much information about short-term fluctuations related to rapid changes of meteorological conditions (especially wind direction). Gas data also permit the modeler to draw connections between receptor model results and those of more traditional dispersion modeling.

Levels of sampling and analysis

From the above discussion it is clear that a wide variety of ambient sampling and analysis methods are available. Below, we recommend three levels of increasing sophistication and cost that parallel the levels given above for determination of compositions of source materials. We assume that most state and local agencies are now equipped with fairly standard monitoring equipment typical of the National Air Surveillance Network (NASN). Although more sophisticated equipment is desirable, some receptor model work is possible with careful use of this equipment. Thus, an agency can start with such equipment and do receptor model studies at fairly reasonable cost and with only
minor changes of procedures and materials. As funds for capital equipment become available, the system can be upgraded to Levels II and III.

**Level I.** This level would entail operation of three or more hi-vol samplers for ≤24-h periods. Preferably, these samplers would be equipped with modern inlet heads and filters with low blank values (i.e., not standard glass fiber filters). Samples would be analyzed for mass, \( \text{SO}_4^{2-} \), and a number of metals by AAS, ICPS, or other chemical methods. Level I also would include standard measurement of the gases \( \text{SO}_2, \text{CO}, \text{O}_3, \) and \( \text{NO}/\text{NO}_x \), and acquisition of meteorological data from the nearest airport or National Weather Service station.

**Level II.** In this level, three or more dichotomous samplers with Teflon filters would be operated for ≤12-h periods. All samples would be analyzed for mass by \( \beta \)-gauge or electrobalance and for elements by XRF. Samples obtained by dichotomous samplers with quartz filters would be analyzed for carbon and ionic species. Pollutant gases would be monitored by high-quality real-time instruments connected to a data-logging system. The network would include at least one meteorological station equipped with a wind vane connected to a data-logger.

**Level III.** This level would encompass all of the systems and measurements listed in Table 1. However, not all of these would need to be added at once. As funds became available, a local agency might wish to equip one key station with as many of the Level III instruments as possible, while maintaining the rest of the network at Level II. As funds permitted, it would be desirable to upgrade at least three stations to Level III to permit use of triangulation in WTA to identify important sources. Note that a number of the Level III methods,
especially those involving minerals, individual particles, vapor-phase species, and organic compounds, are still under development and testing. We anticipate, however, that these methods will have been validated and standardized by the time any agency would be ready to move to complete Level III studies.

SUMMARY AND RECOMMENDATIONS

Receptor model studies of the sources of airborne particles in an area can be initiated at rather small cost with equipment that is much the same as is used in monitoring. The ability of state and local agencies to perform receptor model studies would be greatly enhanced if EPA would provide the best available data on compositions of particles from various types of ubiquitous sources (e.g., coal- and oil-fired power plants, motor vehicles, etc.), receptor model computer packages, and other assistance. Regarding the latter, a whole array of microscopic tools for observing the characteristics of individual particles are just beginning to be exploited. These tools include the analytical scanning electron microscope and the laser microprobe mass analyzer (LAMMA) (Wieser et al., 1980). The use of $^{14}$C, discussed above, is but one example of the measurement of naturally occurring isotopes. In the future, isotopes of many light elements, including B, C (including $^{13}$C), N, O, and S, may prove useful. Thus, although the equipment and methods for receptor model studies have improved enormously over the past few years, the field is still developing, and we can look forward to continued improvements that will enable even more definitive receptor model studies.
We cannot stress too emphatically the need to coordinate meteorological measurements with other field measurements. Receptor modelers, most of whom are basically atmospheric or analytical chemists, have tended to focus on the collection and analysis of chemical species. However, we can greatly enhance the value of data sets by collecting samples over periods sufficiently brief to avoid excessive wind variability and by simultaneously obtaining on-site meteorological data, especially detailed wind direction data.

Acknowledgements—The authors thank the EPA personnel, especially Robert K. Stevens, Thompson G. Pace, and Thomas G. Dzubay, for their excellent services to the receptor modeling community, including design and conduct of the Houston study, provision to the investigators of data from that and the simulated study, and encouragement to all of us to interpret and publish results of this valuable exercise. We also thank our colleagues in the receptor model field for their contributions and suggestions regarding this paper.

REFERENCES


<table>
<thead>
<tr>
<th>Particulate sampler</th>
<th>Flow rate (L min⁻¹)</th>
<th>Filter medium</th>
<th>Species measured</th>
<th>Analytical method(s)¹</th>
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<tr>
<td>Dichotomous</td>
<td>17</td>
<td>Teflon</td>
<td>Mass</td>
<td>β-gauge, gravimetry</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Elements</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ionic species</td>
<td>IC/chemistry</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(SO₂⁻, NO₃⁻, etc.)</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>Nuclepore</td>
<td>Individual particles</td>
<td>SEM/XRF</td>
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<tr>
<td>LBL (Berkeley)</td>
<td>50</td>
<td>Teflon</td>
<td>Crystals, minerals</td>
<td>XRD</td>
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<tr>
<td>dichotomous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hi-vol (possibly</td>
<td>1000</td>
<td>Quartz</td>
<td>Organic compounds</td>
<td>GC/MS, HPLC, etc.</td>
</tr>
<tr>
<td>with cyclcone or size-selective sampling head)</td>
<td></td>
<td></td>
<td></td>
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<table>
<thead>
<tr>
<th>Gas sampler</th>
<th>Species measured</th>
<th>Output</th>
</tr>
</thead>
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<tr>
<td>Total sulfur</td>
<td>SO₂ and other S-containing gases</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>NOₓ</td>
<td>NO, NO₂</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>O₃</td>
<td>O₃</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>CO</td>
<td>CO</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>Polyurethane or</td>
<td>Organic vapors</td>
<td>Later extraction and analysis in laboratory</td>
</tr>
<tr>
<td>other column material</td>
<td></td>
<td></td>
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(continued)

54
Table 1. (continued)

<table>
<thead>
<tr>
<th>Other instrument</th>
<th>Parameter(s) measured</th>
<th>Output</th>
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<tr>
<td>Integrating nephelometer</td>
<td>Light scattering ($b_{scat}$)</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>Condensation nuclei counter</td>
<td>Total particle number concentration (good indicator of fresh combustion aerosol)</td>
<td>Real-time, need data-logging system</td>
</tr>
<tr>
<td>Meteorological tower</td>
<td>Wind speed and direction</td>
<td>Real-time, need data-logging system (should record data at least once per minute)</td>
</tr>
</tbody>
</table>

*Definitions of abbreviations: GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; IC, ion chromatography; INAA, instrumental neutron activation analysis; XRD, X-ray powder diffraction; XRF, X-ray fluorescence; SEM, scanning electron microscopy.*
Table 2. Detectability by XRF and INAA of elements in ambient samples from St. Louis

<table>
<thead>
<tr>
<th>Element</th>
<th>Fine fraction</th>
<th>Coarse fraction</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>XRF</td>
<td>INAA</td>
</tr>
<tr>
<td>Na</td>
<td>Not observable</td>
<td>Strong</td>
</tr>
<tr>
<td>Mg</td>
<td>Not observable</td>
<td>Marginal</td>
</tr>
<tr>
<td>Al</td>
<td>Marginal</td>
<td>Strong</td>
</tr>
<tr>
<td>Si</td>
<td>Strong</td>
<td>Not observable</td>
</tr>
<tr>
<td>P</td>
<td>Marginal</td>
<td>Not observable</td>
</tr>
<tr>
<td>S</td>
<td>Strong</td>
<td>Marginal</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Strong</td>
<td>Strong</td>
</tr>
<tr>
<td>K</td>
<td>Strong</td>
<td>Strong</td>
</tr>
<tr>
<td>Ca</td>
<td>Strong</td>
<td>Marginal</td>
</tr>
<tr>
<td>Sc</td>
<td>Not observable</td>
<td>Strong</td>
</tr>
<tr>
<td>Ti</td>
<td>Marginal</td>
<td>Marginal</td>
</tr>
<tr>
<td>V&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Marginal</td>
<td>Strong</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Marginal</td>
<td>Strong</td>
</tr>
<tr>
<td>Mn</td>
<td>Marginal</td>
<td>Strong</td>
</tr>
<tr>
<td>Fe</td>
<td>Strong</td>
<td>Strong</td>
</tr>
<tr>
<td>Co</td>
<td>Not observable</td>
<td>Strong</td>
</tr>
<tr>
<td>Ni</td>
<td>Marginal</td>
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</tr>
<tr>
<td>Cu</td>
<td>Marginal</td>
<td>Marginal</td>
</tr>
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(continued)
Table 2. (continued)

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*a*May be unobservable because of filter blank.*

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1. Detection limits for XRF and INAA compared with the typical concentration values and ranges of elements in urban air.
1 *To whom requests for reprints of this article should be addressed.

Requests for reprints of the entire series of six articles (including this one) documenting the Quail Roost II workshop should be directed to Robert K. Stevens, MD-47, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, U.S.A.