A FACTOR MODEL OF
URBAN AEROSOL POLLUTION:
A NEW METHOD OF SOURCE IDENTIFICATION

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ABSTRACT

Determination of the sources of suspended particulate matter in the urban atmospheric environment is an important problem in both the study and control of this aspect of air pollution. Recent research has concentrated upon relating sources of airborne particulate matter to measurements of the chemical elements in the aerosol. Methods of source identification through elemental analysis can be divided into two classes: those methods that rely upon the observed mean elemental concentrations, and methods that utilize the intercorrelations of the observed elemental concentrations. The first class includes the mass balance techniques of source identification such as the enrichment factor method and the chemical element balance method. The second class incorporates the correlation techniques such as regression analysis, cluster analysis, and factor analysis.

This dissertation presents a new method of aerosol source identification by elemental analysis that combines for the first time both mass balance and correlation techniques. This is accomplished by applying the mathematical formalism of factor analysis to the chemical element mass balance equations for the aerosol. It is shown that in the urban environment correlations of the chemical elements due to atmospheric dispersion rather than common source ancestry can be eliminated by dividing the elemental concentrations by the total aerosol mass. The correlation matrix of the elements normalized to total mass is subjected to the method of principal factor analysis. The chemical element balance

equations are then put into a form that can be compared to the factor solution. The principal factor solution is rotated by two algorithms developed for this study so that the factors coincide as closely as possible with the initial sources assumed in the chemical element balance. A new source matrix of source elemental compositions is derived from the resulting factors. Finally, the fraction of the aerosol contributed by each source is calculated by reformulating the chemical element balance equations as a linear programming problem. The source contributions along with the source matrix constitute a model of the urban aerosol that accounts for the means, variances, and intercorrelations of the observed elements.

This factor model possesses several important advantages over other techniques. The elemental composition of a source can be deduced from the knowledge of the amount of one element in the material emitted by the source. Also, the presence of an important unknown source can be inferred and its elemental composition estimated. All of this is accomplished by the mechanics of the model; there is very little reliance upon the intuition of the research work.

In order to test the validity of a factor model derived in the manner above, fifteen aerosol samples were collected on .45 micron pore size cellulose acetate filters in the central business district of Portland, Oregon, during September, 1975. The concentrations of Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Pb in the aerosol were determined by X-ray induced, X-ray fluorescence analysis of the samples. The intercorrelations of nine of the elements were analyzed by the principal factor method. Four factors were found to account for over 95% of the observed variance of the elements. These four principal factors were rotated so as to correspond to four sources of aerosol: street dust, metallurgical processes, plating processes, and a hypothetical zinc source whose presence was inferred from the model. Also included in the final model were the automotive and residual fuel oil sources. About 75% of the mass of the aerosol is accounted for by the factor model.

CHAPTER I

INTRODUCTION

The sources and nature of urban air pollution, in general, and aerosols, in particular, have been a matter of concern for centuries (Evelyn, 1661). However, only in the last twenty-five years has there been a concerted scientific approach to the problem. In earlier times the worst sources of air pollution were obvious: the steel mill, smelter, coke oven, etc. Legislation in the late nineteenth and early twentieth century put an end to some of these abuses.

Several well known disasters, such as in London in 1952, made it clear that the public health was in serious danger. In 1955 Great Britian passed strong laws to control smoke, replacing the earlier, ineffective laws. In the United States, Oregon became the first state to enact air pollution legislation in 1951, although the Los Angeles County Air Pollution Control District had been set up by the California legislature in 1947. Major federal legislation was not forthcoming until 1963.

The result of legal and control activity has generally been the elimination of the most obnoxious sources of particulate matter and gases. Yet, it is debatable whether or not the levels of suspended particulate matter have decreased significantly during the last twenty-five years; see, for example, Auliciens and Burton (1973) and Weatherly (1974). The lack of sufficient data for the period in question is one problem.

It is also possible that a downward trend is due to a chance succession of years with favorable meteorological conditions. In any case, at present it is not clear which human activities are predominately responsible for the aerosols found above our cities.

An emission inventory is the method most often used to relate sources of urban pollution to the observed levels of any given pollutant, including aerosols. As the name implys, an emission inventory is a list of all sources of pollution in an area together with an estimate of the amount of each pollutant emitted, usually given in units of tons of pollutant per year. A more detailed outline of the procedures can be found in Danielson (1973). The first comprehensive emission inventory was done for the County of Los Angeles in 1948. As an example, Table I.1 gives the results of a recent emission inventory of the Portland area. Although emission inventories are enormously helpful they ignore some important factors, such as atmospheric chemical reactions and the size distribution of the particulate matter emitted. Also, independent emission inventories seldom agree closely with each other because of lack of standard methods of data collection and reduction.

There exist several methods of attributing aerosols to sources which rely upon direct measurements of the aerosol. Recent research has focused on the use of the elemental composition of the aerosol to determine the sources of the aerosol. The chemical element balance method, which will be described in detail in the next chapter, is one such method which is widely used. In this method source identification is accomplished by the use of simple mass balance relationships for

Table I.1

PORTLAND EMISSIONS SUMMARY (Tons Per Year)

Source	Carbon Monoxide	Hydrocarbons	Oxides of Nitrogen	Oxides of Sulfur	Particulate
1. Industrial					
A. Residual Oil	116	87	2330	5326	670
B. Distillate Oil	18	13	318	122	68
C. Natural Gas	234	41	2409	8	248
D. Process	16559	18479	2106	11582	15353
2. Domestic					
A. Residual Oil	13	10	131	598	75
B. Distillate Oil	309	185	741	1779	618
C. Natural Gas	268	107	1074	8	255
3. Commercial-Inst.					
A. Residual Oil	23	17	230	1050	132
B. Distillate Oil	16	12	163	117	62
C. Natural Gas	63	25	317	2	60
4. Motor Vehicles					
A. Highway	26037	5774	7979	210	609
B. Cruiseway	66295	13045	14542	428	1240
C. Business-Res.	32887	4509	2864	106	308
D. Diesel	4842	807	8071	570	285
5. Airport	2029	1139	369	69	55
6. Open Burning	49	58	6	0	173
TOTAL	149758	44308	43650	21975	20211

From Pitter (1976)

each element. This technique was first applied in Los Angeles in 1968. When used in conjunction with an emission inventory, a fairly clear picture of the sources of the aerosol and their relative importance is given by this method (Friedlander and Gartrell, 1975). The chemical element balance method is not without problems. A detailed knowledge of the elemental composition of each source is necessary but seldom available; thus, entailing a large number of assumptions and approximations. Also, since the method is simply a bookkeeping system for the chemical elements, it has no dynamic or predictive modeling ability.

The purpose of the present research was to extend and generalize the element balance method to a statistical model of an urban aerosol that explains the variability and intercorrelations of the observed chemical elements in the aerosol, as well as their mean values. It was also hoped that the uncertainties in the knowledge of the composition of the sources could be reduced by more efficient use of the available information, particularly the matrix of elemental intercorrelations.

Another major purpose of this study was to demonstrate that the mathematical formalism of factor analysis can be used to produce a physically meaningful model of an urban aerosol. This work presents for the first time a method that relates statistically determined factors to real sources of pollution. This is made possible by the recognition of the relationship of the simple element balance equations to a well known urban diffusion model. The method given here does not require complete knowledge of the elemental composition of all the sources of the aerosol, as does the chemical element balance method. All that is required is that each source of aerosol emit at least one element whose concentration in the aerosol produced by the source is accurately known. The model will then predict the complete elemental composition of the source; this predictive ability is unique to this method. It is stressed that the technique of source identification proposed in this dissertation is purely mechanical in nature. After a hypothesis of the aerosol sources is formulated, the calculations of the model parameters needed to explain the observed data can be entirely programmed for a digital computer.

The basic data set for this study consists of the elemental composition, as determined by X-ray fluorescence analysis, of fifteen samples of Portland urban aerosol obtained during September, 1975. The primary aim was to verify the proposed model, not to characterize the nature of Portland's particulate pollution. Clearly, no general statements on the air quality in Portland are possible with such a limited data set.

Chapter II presents a review of previous work on the identification of aerosol sources from measurements of elemental composition of the aerosol. The aerosol model developed in this study is given in Chapter III. Chapters IV and V describe the experimental methods of aerosol sample collection and the analysis of the samples for elemental composition. Chapter VI presents the result of the application of the model to the data base, and Chapter VII discusses these results.

CHAPTER II

AEROSOL SOURCE IDENTIFICATION BY ELEMENTAL ANALYSIS

INTRODUCTION

It is obvious that rational means to control the ambient levels of suspended particulates in the atmosphere should be based upon the physical nature of the aerosol and a knowledge of the sources of the aerosol. The physical nature of urban and natural aerosols has received much attention and is the subject of two excellent, recent reviews: Willeke and Whitby (1975), and Davies (1974). No similar reviews of the subject of source identification by elemental analysis are available. Since source identification is the eventual goal of this research, this subject is reviewed at length in the following.

The existing methods of source identification can be classified into two groups; those that deal with mean values of elemental concentrations, and those that use the interelement correlations of the concentrations. The first group consists of the chemical element balance method and the enrichment factor method. The second group includes regression analysis, cluster analysis and factor analysis.

MASS BALANCE TECHNIQUES OF AEROSOL SOURCE IDENTIFICATION

The chemical element balance method and the enrichment factor method adopt the same basic assumptions. These are the conservation of mass, the absence of large scale chemical reactions in environmentally occurring processes, and stable source composition. While the conservation of mass is not an unreasonable assumption, the exclusion of chemical reactions is, at times, a serious limitation. Historically, the enrichment factor method is much the older of the two. It has been used widely in geochemistry for many years. The chemical element balance method is due primarily to Dr. Sheldon Friedlander and dates to 1968, see Miller, Friedlander and Hidy (1972).

The enrichment factor method compares the ratios of elemental concentrations in a source and in a sample. Let C_{ij} and C_{is} be the concentration of element i in source j and the sample, respectively. Write

$$M_{i/k,j} = C_{ij}/C_{kj},$$

and

$$M_{i/k,s} = C_{is}/C_{ks}.$$

Thus, $M_{i/k,j}$ is the concentration of element i normalized to element k in source j. The enrichment factor is defined as

$$E = \frac{M_{i/k,s}}{M_{i/k,j}} - 1.$$

Clearly, if the sample is derived entirely from one source then $E = 0$. If there is relatively much more of element i in the sample than in a given source, then E is larger than zero, and one would expect that there is another significant source of the element in the sample. This method is useful when the sample is derived from primarily one source and there are not very many sources present. Urban aerosols do not meet any of the above requirements. Examples of this method are found in Shum (1974), Zoller *et al*. (1974), Bogen (1973) and Struempler (1975). Of special interest is the use of this method by Wesolowski, *et al*. (1973), with time resolved samples, to identify a serious source of lead pollution in the San Francisco Bay area. However, the enrichment factor method, at best, gives qualitative rather than quantitative source information.

The chemical element balance method is more ambitious than the enrichment factor method, and it requires more information about the sources of the aerosol. An extended account of the chemical element balance method is given in the following because it forms a basis for the main topic of this dissertation.

Let P_i be the percentage by weight of element i in an aerosol sample. Assume that there are W sources of element i and that the percentage by weight of element i in source j is a_{ij}. If S_j is the fraction of the aerosol due to source j, the simple mass balance relationship can be written

$$P_i = \sum_{i=1}^{W} a_{ij} S_j . \qquad (1)$$

If n elements are considered, n such equations must be satisfied. Friedlander (1973) includes in equation (1) a factor, f_{ij}, the fractionation of element i due to production of the aerosol by source j. For example, the calcium rich minerals present in soil tend to be less hard than most of the other minerals present in soil. Consequently, soil dust tends to be enriched in calcium relative to bulk soil. Thus, the aerosol derived from soil is also enriched in calcium. Rahn (1976) has done some study of the fractionation problem for soil dust, but this is the only work in the literature on this question. All fractionation effects have been neglected in this work.

There are several limitations of the chemical element balance method; however, two of these are paramount. The elemental composition of the sources must be known quite accurately, and there must be no important secondary sources of the elements in question. Secondary sources are atmospheric chemical reactions that produce aerosols. For example, sulfates in the aerosol are produced predominately by the atmospheric oxidation of sulfur dioxide gas to particulate sulfates. Sulfur could not be included in a chemical element balance because of this important secondary source. The usual products of secondary reactions are sulfates, nitrates and organic compounds. Samples of Portland aerosol analyzied by the Department of Environmental Quality typically contain less than 10% by weight of these species during the summer months. For this reason, secondary sources of aerosol are not considered in this study, although they probably play an important role at other times of the year. Inclusion of secondary aerosol formation is treated in Friedlander (1973); and Tauber (1972) presents a scheme that allows chemical reactions to take place.

In matrix terms, the set of equations (1) can be written

$$P = AS, \tag{2}$$

where P and S are column vectors and A is called the source matrix; the columns of which give the elemental composition, in weight percent, of the sources.

The primary source contributions to the aerosol might be found formally by solving equation (2):

$$S = A^{-1}P. \tag{3}$$

However, it is seldom possible to proceed in such a straightforward manner. The source matrix is generally not accurately known since the elemental composition of the effluent of the various sources is usually obtained from existing data on sources which seldom have the same characteristics as the sources actually present in the airshed. Source sampling is a much better approach, but is not always economically or physically possible. Also, the measured elemental concentrations are subject to sizable experimental errors. Furthermore, the number of sources is usually less than, not equal to, the number of elements included in the analysis. Thus, A is not, in general, a square matrix; therefore, its inverse may not exist. For these reasons the formal solution (3) may not make sense mathematically or physically. Reformulation of the problem is necessary.

The S_i and P_i must obey certain conditions. Obviously, none of the source strengths can be negative or greater than one, i.e.,

$$0 \le S_i \le 1, \text{ for } 1 \le i \le W. \tag{4}$$

If E_i is the error in the determination of element i then equation (1) can be written as

$$P_i + E_i \ge \sum_{j=1}^{W} A_{ij} S_j. \tag{5}$$

The inequality is used to allow for the possibility that a source of element i has not been included in the model. The goal of the element balance should be to account for as much of the aerosol mass as possible, consistent with the assumed number and composition of the sources. Since the S_i are all > 0, the conservation of mass requires that

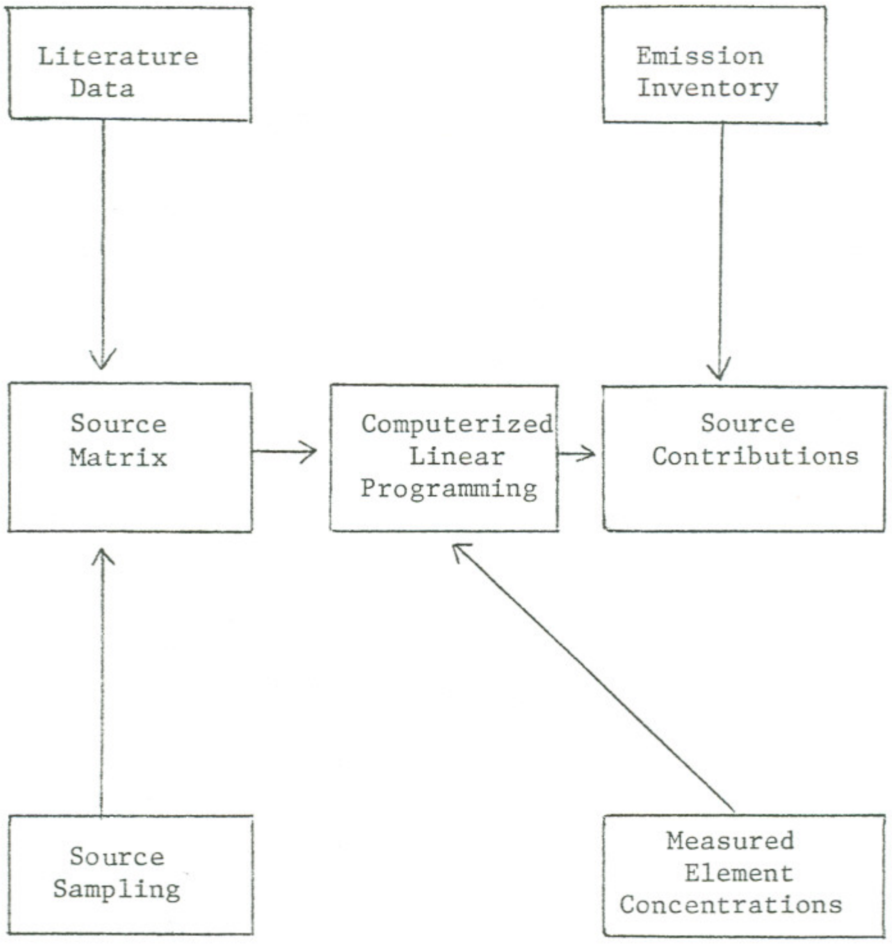
$$0 \leq S_1 + \cdots + S_W \leq 1. \tag{6}$$

Thus, it is only necessary to maximize the linear function,

$$S_1 + \cdots + S_W, \tag{7}$$

which is the fraction of the aerosol accounted for by the mass balance. To summarize, the problem is to determine S_i, $i = 1, \cdots, W$, such that (7) is a maximum, subject to the conditions (4), (5), and (6). This is a classical linear programming problem. Computerized algorithms for its solution are widely available. This method is the one used in this work to obtain solutions to the chemical element balance equations, Figure II.1.

Other methods have been used to find solutions to these equations. Friedlander and Gartrell (1975) obtain a linear least squares solution based on the mass balance equations for certain tracer elements. A tracer is an element that comes either entirely or predominately from one or two sources. Quite often the tracer is also a major elemental constituent of the source. The mass balance equation for a tracer element is very simple. For example, in most areas the only significant source



THE CHEMICAL ELEMENT BALANCE METHOD

Figure II.1

of lead in the aerosol is the combustion of leaded gasoline. The generally accepted value for the fraction of lead in auto exhaust is .4. If 1.1% of the aerosol is lead, the mass balance for lead is written

$$.4S_{auto} = 1.1.$$

This implies $S_{auto} = 2.75\%$.

If there are as many tracer elements as sources, then there is a unique solution for the source strengths. If there are more tracer elements than sources, as in the case considered by Friedlander and Gartrell, then a linear least squares solution to the mass balance equations of the tracers is found. Of course, if there are fewer tracers than sources, then this approach must be abandoned for the linear programming solution.

By the use of an emission inventory it is possible to include the contributions of sources that do not emit any of the elements taken into account by the element balance model. A scale factor, which is the ratio of the emissions of the source not included in the element balance to the emissions of a known source, can be calculated from the emission inventory. The known source strength is then multiplied by this scale factor to determine the unknown source strength. As an example, diesel powered vehicles constitute an aerosol source that does not emit any of the analyzable elements in this study. From an emission inventory, the ratio of the emissions of diesels to leaded gasoline powered vehicles is found to be .1, say. Using the example given above, the calculated auto source strength based upon lead is 2.75%. Thus, the fraction of the aerosol due to diesels scales to .275% of the total aerosol mass.

The work of Gatz (1975) on the Chicago aerosol provides an interesting example of the chemical element balance method. Table II.1 gives the source matrix assumed by Gatz and the composite elemental composition that he attributes to the Chicago aerosol. Gatz uses the tracer element approach to choose various scenarios of source contributions and compares them by evaluating how well the predicted elemental concentrations agree with those assumed for the composite aerosol. The tracer elements used by Gatz are: lead, automotive; manganese, iron and steel manufacture; aluminum, soil and coke production; calcium, cement production; vanadium, fuel oil combustion. The final results of Gatz are given in Table II.2 along with results for the Los Angeles aerosol, for comparison.

One criticism of Gatz's work is the fact that the listed sources do not correspond to real sources. In particular, the soil dust source is in reality primarily a street dust source. It is now recognized that street dust reentrained by wind and vehicular traffic is a major contributor to urban aerosol loadings (Hana and Gilmore, 1975, and Cowherd, *et al*., 1976). Since street dust is enriched relative to soil dust in such elements as lead, zinc, and calcium, the element balance is significantly affected. The need for a cement source is eliminated entirely because all the calcium can be explained as being derived from street dust (see Table VII.1 of this dissertation for an example).

Table II.1

adapted from Gatz (1975)

EXAMPLE OF CHEMICAL ELEMENT BALANCE

			Elemental Concentrations in Source Materials (percent by weight)			Composite Chicago Aerosol (percent by weight)	
Element	Auto	Cement	Coal & Coke	Fuel Oil	Iron & Steel	Soil	Composition
Al		2.5	14.0	5.0	2.4	5	2.0
As			0.016				0.02
Br	7.9						0.2
Ca		44	4.0	0.4	5.4	0.8	2.0
Cd			0.004				0.01
Cl	6.8						3
Co			0.009	0.15		0.002	0.004
Cr			0.03	0.12		0.005	0.006
Cu			0.04	0.16	1.6	0.003	0.1
Fe	0.4	2.7	7.0	2.5	38.7	3.0	3
Hg			0.00002				0.004
K				0.10		2.0	0.8
La						0.004	0.002
Mg		1.2	0.8	0.3	1.6	0.7	0.9
Mn			0.024	0.03	2.4	0.03	0.1
Na			0.4	1.5		0.6	0.4
Ni			0.04	6.0		0.005	0.025
Pb	40		0.12	0.18		0.005	1.1
Sc						0.0015	0.00072
Ti			0.9	0.03		0.3	0.01
V			0.08	2.5		0.007	0.04
Zn	0.14		0.09	0.05	1.8	0.01	0.6

Table II.2

adapted from Gatz (1975), Gartrell and Friedlander (1975), and Hammerle and Pierson (1975)

SOURCE CONTRIBUTIONS TO ATMOSPHERIC AEROSOL

(weight percent)

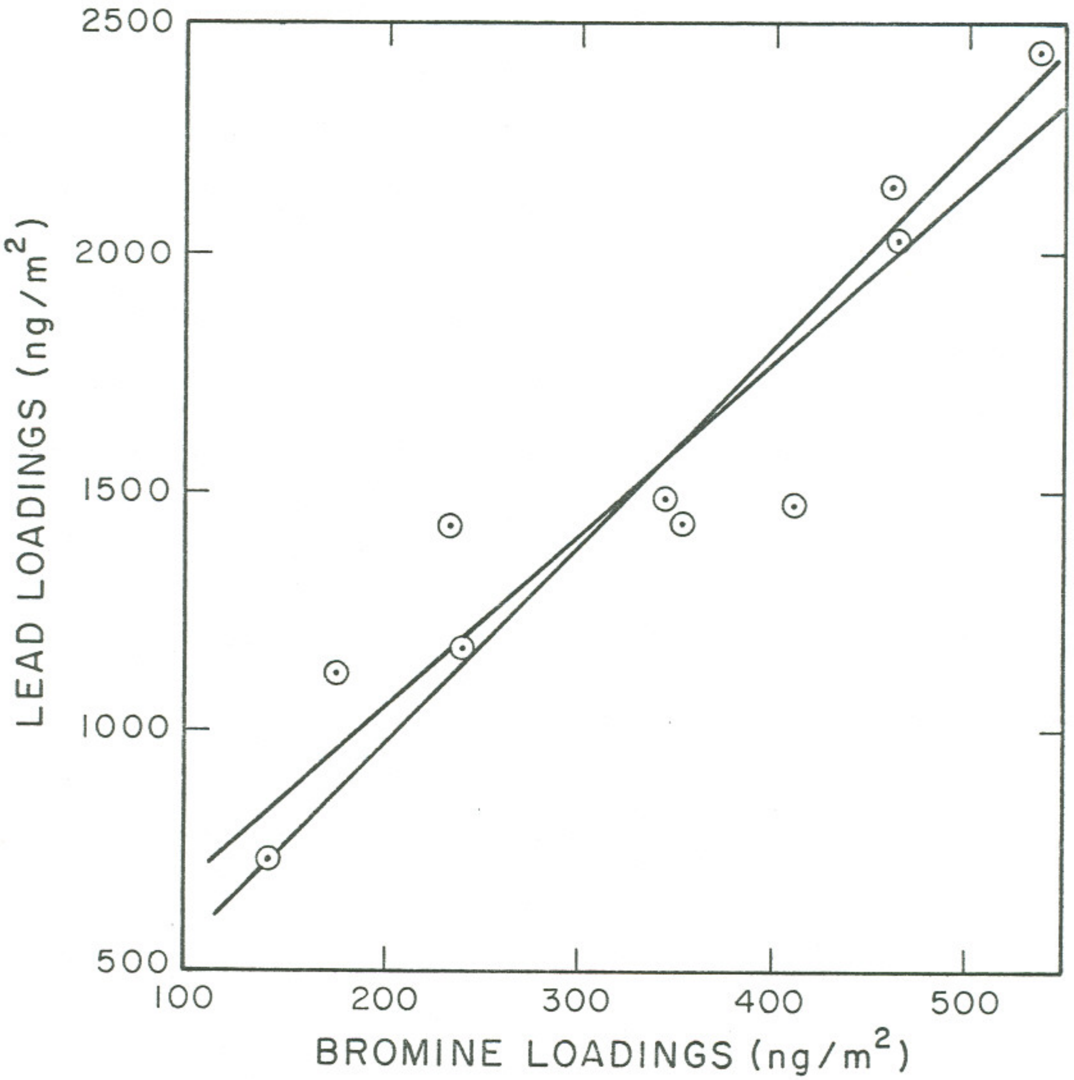
Source	Chicago	Pasadena 9/29/72	Pasadena 11/16-27/72
Sea Salt	-	1.1	-
Soil Dust	18	31	20
Auto Exhaust	2.8	8	18
Cement	3.2	2	0.3
Fuel Oil	1.4	0.2	< .3
Steel	3.9	< 5.5	-
Total	29.3	47.8	38.6

CORRELATION TECHNIQUES OF AEROSOL SOURCE IDENTIFICATION

As stated in the introduction, the other class of source identification methods include those which rely mainly upon the correlations of the elements measured in the aerosol; these are regression analysis, cluster analysis and factor analysis. The basic idea of all the correlation based methods is simply that if two elements come from one source, then their observed loadings in the aerosol should be correlated to some extent. These methods have two advantages over the mass balance techniques discussed above. Systematic errors in the experimental determination of the elemental composition of the aerosol are unimportant in these methods. This is because the elemental correlations are only dependent on variations of the concentrations from the mean. Also, these methods do not usually require any detailed information on the elemental composition of the sources. The major disadvantage of the correlation methods is the fact that correlations of independent elements can be introduced by the common effects on ambient elemental concentrations of changes in meteorological variables that effect atmospheric dispersion. Another problem of these techniques is their inability to quantitatively relate the sources deduced from the analysis and the actual aerosol sources.

Regression analysis is the simplest correlation method, it is somewhat comparable to the enrichment factor method. In a situation in which one source dominates all others it seems to be the most natural method of analysis. An excellent example of the phenomenon is shown by the observed values of lead and bromine aerosol loadings near a highway. Figure II.2 is a plot of such data obtained during a recent investigation at this institution of the effects of highways on air quality (Baum and Pitter, 1976). The lines shown in the figure are the regression, or linear least squares, lines for this data. The two lines correspond to considering lead and bromine, respectively, as the independent variable. Note that regression analysis predicts only that lead and bromine come from the same, or highly correlated, sources. Further information is necessary to identify automobiles as the source in question; for instance, the ratio of lead to bromine in leaded gasoline. In other cases, where there are several independent sources of an element, the regression analysis may not be as conclusive. In such cases multiple correlation analysis may present a useful extension of the simple regression analysis. Baum, Henry and Pitter (1974) presents an example of such an analysis.

Cluster analysis and factor analysis represent more sophisticated statistical methods of correlation analysis than regression techniques. Cluster analysis is a statistical method that attempts to define groups of elements with high intercorrelations among the group members. These groups are referred to as clusters. The assumption is that each cluster of elements corresponds to a source of aerosol. No quantitative relationship is given to link the clusters with real sources. The mathematical details of cluster analysis can be found in Everitt (1974). Applications of cluster analysis to aerosol source identification are made in John *et al*. (1972), Gaarenstroom et al. (1976) and Neustadter *et al*. (1976). Factor analysis is closely related to cluster analysis in its intuitive approach to the data.



LEAD AND BROMINE IN PARTICLES 1.4-0.4 MICRONS IN DIAMETER

Figure II.2

Because factor analysis is central to the model presented here, it will be discussed in considerable detail below.

PRINCIPLES OF FACTOR ANALYSIS AND THE PRINCIPAL FACTOR SOLUTION

The purpose of this subsection is to present the results of factor analysis that are necessary to the development of the aerosol model of Chapter III. If a result can be derived simply and instructively, then the derivation is given. However, no attempt has been made to present a complete account or proof of all the methods of factor analysis that are presented below. In particular, a full development of the principal factor solution is beyond the scope of this thesis; the interested reader is referred to Harmon (1967), an excellent reference on factor analysis. A shorter exposition by the same author can be found in Ralston and Wilf (1968).

Factor analysis utilizes a multivariate linear model of the form

$$C_i = \sum_{j=1}^{m} \alpha_{ij} F_j + d_i U_i \ . \tag{8}$$

The n observed variables, C_i, are assumed to be linear combinations of m (usually much smaller than n) common factors, F_j, and unique factors, U_i. The common factors account for the correlations among the observed variables, while the unique factors account for any remaining variance, usually experimental error. The problem is to determine the α_{ij} and d_i from the mean, variance, and correlations of the C_i.

In the terminology of factor analysis, the α_{ij} are referred to as the factor loadings. It is assumed that C_i, U_i, and F_j are all random variables in standard form, i.e., mean zero and variance one. If not, the transformation

$$\tilde{x} = (x - \mu_x)/\ \sigma_x ,$$

where μ_x and σ_x are the mean and standard deviation of x, will reduce any variable to standard form. The reduction to standard form simplifies the analysis greatly. Let μ_{c_i} and σ_{c_i}, as usual, be the mean and standard deviation of C_i. E(x) is the expected value of x, i.e.,

$$E(x) = \int_{\infty}^{\infty} xf(x)dx,$$

where f(x) is the probability distribution of x. The correlation of C_i and C_j is given by Feller, (1957) as

$$r(C_i,C_j) = E[(C_i - \mu_{C_i})(C_j - \mu_{C_j})]\ (\sigma_{C_i}\sigma_{C_j})^{-1}. \quad (9)$$

This relation defines the correlation matrix of the n observables. This matrix is n dimensional, square, symmetric, and positive definite. The correlation matrix is estimated form L observations of the C_i's by the formula:

$$r(C_i,C_j) = (S_iS_j)^{-1} \sum_{k=1}^{L} (C_{ik} - m_i)(C_{jk} - m_k),$$

where

$$C_{ik} = k^{th} \text{ observation of variable } i,$$

$$m_i = \text{sample mean of variable } i$$

$$= L^{-1} \sum_{k=1}^{L} C_{ik},$$

and

S_i = sample standard deviation of variable i

$$= \left[(L - 1)^{-1} \sum_{k=1}^{L} (C_{ik} - m_i)^2 \right]^{1/2} .$$

The correlation matrix contains all the information available about the interactions of the variables. But the common factors are meant to explain these interactions through the matrix of the α_{ij}. Thus, the α_{ij} matrix must be calculated from the correlation matrix. Just how this is done is presented at the close of this section, after a number of properties of the factor analysis model have been derived.

Since the variables are in standard form $\mu_{c_i} = \mu_{c_j} = 0$, and $\sigma_{c_i} = \sigma_{c_j} = 1$. Thus equation (9) gives

$$r(C_i,C_j) = E(C_iC_j).$$

The factors are usually assumed to be pairwise independent, i.e.,

$$E(F_iF_j) = E(U_iU_j) = \delta_{ij} = \begin{cases} 0 \text{ if } i \neq j \\ 1 \text{ if } i = j \end{cases} , \qquad (10)$$

and

$$E(U_iF_j) = 0 \text{ for all i and j.}$$

Equations (8) and (10) can be used to give an intuitive interpretation to the α_{ij}, the factor loadings. The correlation of the observed variable C_i with factor F_j is

$$r(C_i,F_j) = E\left[F_j\left(\sum_k \alpha_{ik}F_k + d_iU_i\right)\right]$$

$$= \sum_k \alpha_{ik} E(F_j F_k) + d_i E(F_j U_i)$$

$$= \alpha_{ij} \qquad (11)$$

Therefore, α_{ij} is just the correlation of variable i with factor j.

It is also interesting to calculate the correlation of C_i and C_j in terms of the factors:

$$r(C_i, C_j) = E\left[(d_i U_i + \sum_k \alpha_{ik} F_k)(d_j U_j + \sum_k \alpha_{jk} F_k) \right]$$

$$= \sum_k \alpha_{ik}\alpha_{jk} \underbrace{E(F_k^2)}_{1} + \sum_{k \neq \ell} \alpha_{j\ell}\, \alpha_{ik} \underbrace{E(F_k F_\ell)}_{0} + \sum_k \alpha_{jk} \underbrace{E(U_i F_k)}_{0}$$

$$+ \sum_k \alpha_{ik} \underbrace{E(F_k U_j)}_{0} + d_i d_j E(U_i U_j)$$

$$= \sum_k \alpha_{ik}\alpha_{jk} + d_i d_j \delta_{ij}. \qquad (12)$$

Equation (12) is important for several reasons. First, note that if $C_i = C_j$ then $r(C_i, C_j)$ is the variance of C_i, which is one, i.e.,

$$\sigma^2_{c_i} = r(C_i,\ C_i) = \sum_k \alpha^2{}_{ik} + d_i^2 = 1. \qquad (13)$$

Thus, α^2_{ik} is the portion of the variance of C_i due to the common factor F_k. If U_i is the experimental error, then d_i^2 is the portion of the variance of C_i due to this error.

The second important observation to make about equation (12) is that if α_{ik} and α_{jk} are considered to be the elements of two vectors, $\vec{C}_i$ and $\vec{C}_j$, in the m-dimensional space spanned by the orthogonal vectors,

F_k, then the correlation of C_i and C_j is the dot product $\vec{C}_i \cdot \vec{C}_j$. Geometrically, this means that the correlation of C_i and C_j is the cosine of the angle between the two vectors. By the same analogy, the length of the vector $\vec{C}_i$ is $(\sum_k \alpha_{ik}^2)^{1/2}$, the amount of the standard deviation of C_i due to the common factors.

Thirdly, assuming that the correlations of the measured quantities are known, equation (12) gives $n(n + 1)/2$ conditions that the n^2 α_{ij} must satisfy. Clearly, the factor model is not uniquely determined by the conditions of the problem. There are an infinite number of solutions for the α_{ij} that will explain the observed correlations of the measurements in terms of sums of independent factors.

One method to determine a unique set of α_{ij}'s is to define a function of the α_{ij}'s; the set of α_{ij} that produces an extreme value of this function is thus uniquely determined. One particularly important factor solution obtained in this manner is the principal factor, or principal component solution. It is arrived at by defining the function

$$V_j = \sum_{k=1}^{m} \alpha_{kj}^2 \ .$$

Recall from equation (13) that α_{kj}^2 is the variance of observable k due to common factor j. Thus, V_j is the total contribution of factor F_j to the variance of all the observed variables. It can be shown (Harmon, 1967, Chap.8) that the set of α_{ij}, $i = 1,n$ that maximizes V_j is just the eigenvector of the correlation matrix corresponding to the largest eigenvalue. This eigenvector must be divided by the square root of its eigenvalue if it is to have a variance, or length, of one. This set of α_{ij}'s is unique in that it accounts for a maximum of the variance of all the variables. It can also be shown that the eigenvector corresponding to the second largest eigenvalue explains a maximum of the variance not accounted for by the first eigenvector, and so on. Thus, the eigenvectors of the correlation matrix, ordered by their eigenvalues and normalized by multiplying by the square root of their respective eigenvalues, represent one possible solution to the factor analysis problem, ignoring possible unique factors.

The primary use of the principal factor solution is to reduce the dimensionality of the factor solution. In many cases it is noted that only the first few factors are needed to account for most of the variance of the observables. Thus, the number of factors can be reduced without significant loss of information. It is for precisely this reason that the principal factor solution is later used as the starting point in the development of the urban aerosol model.

The following is a recapitulation of how to find the principal factor solution for the α_{ij} from the correlation matrix, assuming there are no unique factors. First, the correlation matrix must be calculated from the observations of the C_i. Next, one must solve for the eigenvalues and eigenvactors of the correlation matrix. Each eigenvector is normalized by multiplying it by the square root of the corresponding eigenvalue. The resulting vectors are then the columns of the matrix of the α_{ij}. Appendix A presents this approach applied to a set of data produced by a Monte Carlo simulation of four observables derived from two factors. The necessary results of factor analysis are not at hand to be used in Chapter III. The remainder of this chapter is devoted to a brief discussion of the previous attempts to apply factor analysis to air quality data.

As noted in Prinz and Stratmann (1968), there are two possible applications of factor analysis to air quality data. It may be used, as in this study, to investigate the basic nature of the relationships among variables that influence air quality. The other type of application would be to establish certain groupings of observations or variables that can be used to classify air quality data into a number of regimes. Almost all the previous work in this area has attempted to both classify the data and use this classification to study the basic nature of the phenomenon. Blifford and Meeker (1967), Laamanen and Partanen (1969) and Peterson (1970) have used factor analysis to investigate spatial variations in urban air quality data. The more recent studies have concentrated on using factor analysis to relate temporal variations in aerosol element concentrations to source characteristics; the references are: John et al. (1972), Hopke et al. (1976), and Gaarenstroom et al. (1976). Analysis of time series data by factor analysis is very clearly explained in Vavilova et al. (1969).

CHAPTER III

A FACTOR MODEL OF URBAN AEROSOLS

INTRODUCTION

The aerosol model developed below is an attempt to combine, for the first time, mass balance and correlation techniques of aerosol source identification. Specifically, it is desired to extend the chemical element balance method, by means of factor analysis, to a model that can relate the means, variances, and correlation of aerosol elemental concentrations to real sources of aerosol in the urban environment.

There are two fundamental obstacles to the attainment of this goal, and both are overcome in the same manner. First, the chemical element balance model is a first order model. It is a simple statement that in any given period the average amounts of elements in the aerosol must obey mass balance conditions. There is no prediction of any second order effects, such as variances and correlations, because these variations are due primarily to atmospheric dispersion which is not included in the model. Secondly, the factor analysis suffers from intercorrelations of elements introduced by variability in atmospheric dispersion that tend to mask the intercorrelations due to a common source ancestry. It is shown below that the solution to both of these problems is to divide the absolute elemental concentrations by the total aerosol mass. This simple normalization removes the effects on elemental concentrations of atmospheric dispersion in an urban area. The remaining variability in the data is due to actual source strength variations and variation in wind direction which changes the mix of sources contributing to the particulate loading at any given receptor.

URBAN DISPERSION MODELLING AND THE CHEMICAL ELEMENT BALANCE

The model of urban atmospheric dispersion assumed in this analysis is that of Gifford and Hana (1971). This model applies to area sources of pollutants, i.e., those sources that can be considered to be emitted from a geographical area as a whole rather than as individual point or line sources. However, Scorer (1968), pp. 40-41, points out that sufficiently far downwind, the dispersion of pollutants from a point source is equivalent to the dispersion from an area source. Thus, the validity of the model does not suffer if large point sources are not located near the sampling site.

The Gifford-Hana model ignores lateral diffusion entirely in favor of the advection of pollutants by the wind. Diffusion in the vertical direction is allowed and is assumed obey the steady state diffusion equation in two independent variables,

$$u(z)\frac{\partial C_i}{\partial x} = \frac{\partial}{\partial z} K(z)\frac{\partial C_i}{\partial z} , \qquad (1)$$

where z is the vertical dimension, x is the distance down wind from the edge of the area source, C_i is the pollutant concentration, and u(z) the wind speed. K(z) is the eddy diffusivity as defined in the K theory of turbulent diffusion. For an excellent discussion of this theory and the derivation of equation (1), see Seinfeld (1975). It is further assumed that the following power law hold for σ_z, the vertical dispersion coefficient.

$$\sigma_z = ax^b ,$$

where the parameters a and b depend upon meteorological condition, see Counehan (1975). The solution to equation (1) under the given conditions is

$$C_i = \left(\frac{2}{\pi}\right)^{1/2} Q_0 x^{1-b} \left[a(1 - b)u\right]^{-1}. \tag{2}$$

Q_0 is the area source strength in units of $g/m^2/sec$. Let

$$G = \left(\frac{2}{\pi}\right)^{1/2} x^{1-b} \left[a(1 - b)\right]^{-1} , \tag{3}$$

then equation (2) becomes

$$C_i = GQ_0 /u . \tag{4}$$

Gifford and Hana propose that this very simple model be taken seriously because its predictions agree just as well with observation as the predictions of more complicated models (Gifford and Hans, 1975). Also, Gifford and Hana (1973) demonstrate that for a number of cities the dimensionless parameter, G, of equation (4) is approximately constant. Although the data do not allow the exact form of the dependence of G on atmospheric stability to be deduced, the fact that the same value is obtained in many different cities supports their assertion that equation (4) successfully models urban dispersion. Further support for the Gifford-Hana model is found in Kleinmann et al. (1974, 1976). It is shown that concentrations of total suspended particulate and some trace metals in New York City are indeed inversely proportional to dispersion, as measured by the product of wind speed and inversion height.

Knox and Lange (1974) have tested the validity of equation (4) in a very interesting manner. They point out that if G and Q_0 are kept constant, then all of the variation of C_i is due to 1/u. Thus, the frequency distribution of C_i should be identical in form to that of 1/u. This comparison was made using hourly carbon monoxide and wind speed data for San Francisco. The agreement of the model and observation was excellent, showing the validity of the Gifford-Hana model when interpreted statistically. An account of the theory fundamental to this research is given in Pollack (1973).

The significance of the Gifford-Hana urban diffusion model to the chemical element balance model and the factor analysis of elemental aerosol data is developed below. Let T be the total aerosol source strength from all area sources in units of $\mu g/m^2/sec$ and let M be the total aerosol mass in $\mu g/m^3$. Equation 4 predicts

$$M = (G/u)T.$$

If

$$D = G/u \quad , \tag{5}$$

then

$$M = DT. \tag{6}$$

D is a dispersion parameter with units of $(m/sec)^{-1}$. It is now possible to derive the chemical element balance equations from the Gifford-Hana model as follows. Let a_{ij} be the fraction of the element i in area source j. Then, if the source strengths are Q_i, equation (4) and (5) yield

$$C_i = \sum_{i=1}^{w} a_{ij} Q_j D \ , \qquad (7)$$

where C_i is the concentration of element i in $\mu g/m^3$. Let S_j be the fraction of the total aerosol mass due to the source j. Then,

$$Q_j = S_j T \ .$$

Making these substitutions in equation (7),

$$C_i = \sum_{i=1}^{w} a_{ij} S_j DT \ .$$

Using equation (6),

$$C_i = \sum_{i=1}^{w} a_{ij} S_j M \ . \qquad (8)$$

This equation is a slight variant of the chemical element balance equation (1) of Chapter II. However, it is now clear that the effects of atmospheric dispersion are incorporated in the total mass of the aerosol.

The above equation can be used to investigate the intercorrelations of observed elemental concentrations due to variations in meteorology. Consider two elements, write equation (8) for each,

$$C_1 = Y_1 \ M, \text{ and}$$

$$C_2 = Y_2 \ M,$$

where

$$Y_1 = \sum_{j=1}^{w} a_{1j} S_j , \text{ and}$$

$$Y_2 = \quad a_{2j}S_j \ .$$

Assuming that Y_1, Y_2 and M are independent, it is shown in Appendix B that correlation of C_1 and C_2 is

$$r(C_1,C_2) = e_{Y_1}e_{Y_2}/[(1 + e_{Y_1}^2 + e_M^2)(1 + e_{Y_2}^2 + e_M{}^2)]^{1/2}, \quad (9)$$

where $e_x = \mu_x/\sigma_x$, the ratio of the mean of x to its standard deviation. A simplification of (9) that is often realistic results from assuming that

$$e_M = e_{Y_1} = e_{Y_2} = e.$$

Equation (9) becomes

$$r(C_1,C_2) = \frac{e^2}{1 + 2e^2} = \frac{1}{2 + 1/e^2} \ .$$

As e gets large $r(c_1,c_2)$ goes to 0.5. It is shown later that $e = 5$ is a reasonable value; for this number $r(c_1, c_2) = .49$. The conclusion of this exercise is that if the basic model is valid, then virtually all elements should correlate at about the .5 level of higher, even if their sources are uncorrelated! A high degree of correlation of all elements in the aerosol has indeed been noted by Hamerle and Pierson (1975) in Los Angeles. The above analysis would explain this observation.

If one element's concentrations are not correlated highly with every other element before normalization by the total mass, then the measurements of that element are probably affected by some anomaly. For example, the element may be present in amounts near its minimum detectable limit; in this case the measurements are mostly noise, which does not correlate with anything. Further examples will be given in Chapter VI.

Clearly, the basic assumptions of a factor model based on the chemical element balance equations must include the requirements for the applicability of the Gifford-Hana dispersion model. The following is a collection of all the assumptions necessary for these two models to apply.

(0) Mass is conserved.

(1) There are no secondary or background sources of aerosol.

(2) The chemical composition of the sources remains constant.

(3) The mass fraction of at least one element is known for each source.

(4) There are no fractionation effects on the aerosol produced by a source.

(5) Lateral diffusion of pollutants is neglected.

(6) Vertical diffusion obeys the turbulent diffusion equation.

(7) All sources of aerosol can be considered to be area sources.

Assumption (3) follows from the mathematical development of the model in the next section.

DEVELOPMENT OF A FACTOR MODEL OF URBAN AEROSOLS

The above section has cleared the way theoretically for the combination of the chemical element mass balance technique with the factor analysis approach, which is the chief aim of this work. The actual details of this melding, presented below, constitute the original results of this dissertation.

It is assumed that the means, variances, and correlations of a number of elements, expressed as a percentage of the total aerosol mass, are available. Furthermore, it is assumed that an initial matrix of source compositions, such as is necessary for a chemical element balance, is at hand; and that the principal factor solution has been obtained from the correlation matrix by the methods given on page 28.

The chemical element balance equations and an assumed initial source matrix of source compositions are put into standard form, i.e., all the variables are reduced to mean zero and standard deviation one. The standardized sources are expressed as linear combinations of the principal factors. The principal factor solution is then rotated to roughly align the principal factors with the assumed standardized sources. Next, a criterion is found to assess the degree of alignment of the standardized sources and a factor. Using this criterion, the factors are again rotated so as to align with the standardized sources as closely as possible. The final factor solution is then converted to unnormalized form. The result is a chemical element mass balance model that describes all the observed means, variances, and correlations of the elements.

The first step in the procedure outlined above is the standardization of the chemical element balance equations. All the variables must be put in standard form, i.e., mean zero and variance one. Repeating equation (1), Chapter II,

$$P_i = C_i/M = a_{i_1}S_1 + \cdots + a_{iw}S_w \ . \tag{10}$$

Again let μ_x and σ_x be the mean and standard deviation of x. Add and subtract $a_{i_1}\mu_{s_1}$, $a_{i_2}\mu_{s_2}$, etc. to equation (10) to get

$$P_i = a_{i_1}(S_1 - \mu_{s_1}) + \cdots + a_{iw}(S_w - \mu_{sw}) + a_{i_1}S_1 + \cdots + a_{iw}S_w \ ,$$

but

$$\mu_{P_i} = a_{i_1}\mu_{s_1} + \cdots + a_{iw}\mu_{sw} \ .$$

Using this and multiplying and dividing each term by σ_{si} yields

$$P_i - \mu_{P_i} = a_{i_1}S_1\left(\frac{S_1 - \mu_{s_1}}{\sigma_{s_1}}\right) + \cdots + a_{iw}S_w\left(\frac{S_w - \mu_{sw}}{\sigma_{sw}}\right).$$

Now divide both sides by σ_{P_i}, and let $\tilde{x}$ denote a variable in standard form. The above expression becomes

$$\tilde{P}_i = \frac{P_i - \mu_{P_i}}{\sigma_{P_i}} = \sum_{j=1}^{w}\left(\frac{a_{ij}\sigma_{sj}}{\sigma_{P_i}}\right)\tilde{S}_j \ . \tag{11}$$

If the standardized sources are considered to be factors, then

$$\alpha_{ij} = a_{ij}\sigma_{sj}/\sigma_{P_i} \ , \tag{13}$$

or

$$a_{ij} = \alpha_{ij}\sigma_{P_i}/\sigma_{sj} \ , \tag{13a}$$

where the α_{ij} represent factor loadings. Equations (13) and (13a) are basic relations that are used to relate the composition of a source to the factor loadings corresponding to that source and vice versa. Let S_o be a source of known composition, that is, its a_{oj} are known. The value of σ_{P_i} and σ_{S_o} can be estimated from the experimental data, as shown in the example on page 42. The corresponding factor loadings, α_{oj}, are calculated from equation (13). Conversely, if the factor loadings are known then it is possible to calculate the corresponding source composition using (13a), if an estimate of σ_{S_o} is found. To this end, rewrite (13) as

$$\sigma_{S_o} = \alpha_{oj}\sigma_{P_i}/a_{oj} \; . \tag{13b}$$

If the amount of one element in the source is known, then this value of a_{oj} can be used in (13b) to calculate σ_{S_o}. The resultant value of σ_{S_o} can then be substituted in (13a), along with the factor loadings, to deduce the remaining elemental composition of the source corresponding to the factor. Thus, in order to relate a set of factor loadings to the elemental composition of a source it is necessary to know a priori the amount of at least one element in the source. This assumption has already been stated on page 36.

A connection has now been demonstrated between the matrix, α_{ij}, of the factor model and the source matrix, a_{ij}, of the chemical element balance model. But the factor loadings are calculated from the interelement correlations, thus a relationship has also been found between the correlation matrix and the source matrix. It remains to be shown how the information in the correlation matrix is transmitted via the factor loadings to produce a new source matrix that is consistent with the observed correlations. In order to accomplish this the factors must be rotated so as to correspond to real sources of aerosol.

$\tilde{S}_o$ is the column vector made up of the α^S_{oj} as determined from the source matrix from equation (13). Then $\tilde{S}_o$ is referred to as a source factor, or a standardized source. In order to aline a factor with the standardized source, it is expressed as a linear combination of the factors

$$\tilde{S}_o = \sum_{j=1}^{W} d_{oj} F_j \ , \tag{14}$$

the correlation with element k is

$$r(\tilde{S}_o, \tilde{P}_k) = E(\tilde{S}_o \tilde{P}_k) \quad .$$

Recall from Chapter II equation 9 that the correlation of element j with source S_o is the factor loading α^S_{ok}. Using equations (11) and (14)

$$\begin{aligned} \alpha^S_{ok} &= r(\tilde{S}_o, \tilde{P}_k) = E[(\sum_j d_{oj} F_j)(\sum_j \alpha_{kj} F_j)] \\ &= \sum_j d_{oj} \alpha_{kj} \ . \end{aligned} \tag{15}$$

If there are n elements, then (15) defines n equations to be satisfied by the W d_{oj}'s. There are usually more elements than factors, so the last set of equations is overdetermined. The least squares approach is used to determine the d_{oj} so that the expression

$$\sum_k (\alpha^S_{ok} - \sum_j d_{oj} \alpha_{kj})^2$$

is a minimum. This solution is given by the standard least squares formulae

$$\vec{D} = \overleftrightarrow{A}^{-1} \vec{B} \quad , \qquad (16)$$

where

$$A_{mn} = \sum_i \alpha_{im} \alpha_{in} \quad ,$$

$$B_m = \sum_j \alpha_{jm} \alpha^{S}_{oj} \quad ,$$

and D is the column vector of the d_{oj}. Geometrically, the d_{oj} are the coordinates of the source factor, $\tilde{S}_o$, in the factor space. The goal is to have one of the factors, i.e., one of the coordinate axis, coincide exactly with $\tilde{S}_o$. This is achieved by rotating the principal factors so that all but one of the d_{oj} are reduced to zero. A specific example of this procedure follows in the next paragraph. Table III.1 contains a summary of the above relations between the factor space and the sample space.

An example may make the procedure more clear. Entrained street dust is seen in Chapter VI to be a major aerosol source in Portland. Silicon is a major constituent of street dust, and street dust is the only major source of silicon in the aerosol. Thus, silicon can be used as a tracer for street dust. The facts that make silicon a good tracer also imply that the correlation of the street dust factor and silicon should be high, say .95. Equation (13b) can be used to estimate σ_{Dust}, the standard deviation of the dust source. If

$$\alpha_{Si,\ Dust} = .95 \ ,$$

$$\sigma_{Si} = 0.36\% \text{ (from Table VI.2)},$$

and

$$a_{Si,\ Dust} = 20\% \text{ (from Table V.4)};$$

then

$$\sigma_{Dust} = \frac{\alpha_{Si,\ Dust}\sigma_{Si}}{a_{Si,\ Dust}} = .0646$$

This value of σ_{Dust} can now be used with the elemental concentrations of average dust in Table V.4 to calculate the expected factor loadings for street dust from equation (13b), the results are,

Al	0.55
Si	0.95
K	0.633
Ca	0.472
Fe	0.555
Cr	0.009
Mn	0.231
Ni	0.026
Zn	0.032

These numbers are the α^{S}_{oj} in equation (16), and the column vector formed by them is $\tilde{S}_o$, the loadings of a standardized street dust factor. The principal factor solution for the correlation matrix of these elements, obtained for this study, is given in Table VI.6.

Table III.1

BASIC CONCEPTS OF THE FACTOR MODEL

Concept	Sample Space		Factor Space
	Unnormalized	In Standard Form	
Variable	P_i (percentage of element i in the aerosol)	$\tilde{P}_i = \frac{P_i - \mu_{P_i}}{\sigma_{P_i}}$	$\tilde{P}_i$
Dimension	n	n	W ($\leq$ n)
Coordinates $i = 1, \cdots, N$ $j = 1, \cdots, Y$	P_{ij} (jth observation of variable P_i)	$\tilde{P}_{ij}$	σ_{ij} (correlation of element i and factor j)
Linear Model $k = 1, \cdots, z$	$P_i = \sum_k a_{ik} S_k$ (chemical element balance)	$\tilde{P}_i = \sum_k \frac{a_{ik}\sigma_{sk}}{\sigma_{Pk}} \tilde{S}_k$	$\tilde{P}_i = \sum_{j=1}^{w} \alpha_{ij} F_j$
Correlation of Variables i and j	$\frac{\sum_{\ell=1}^{y} (P_{i\ell} - \mu_{P_i})(P_{j\ell} - \mu_{P_j})}{(n-1)\sigma_{P_i}\sigma_{P_j}}$	$\frac{\sum_{\ell=1}^{y} \tilde{P}_{i\ell}\tilde{P}_{j\ell}}{n-1}$	$\sum_{\ell=1}^{w} \alpha_{i\ell}\alpha_{j\ell}$
Relationship, of Sources and Factors			$\tilde{S}_i = \sum_{j=1}^{w} d_{ij} F_j$ (d_{ij} = correlation of source i and factor j)

The least squares solution in equation (16) gives the following coordinates of the dust factor in terms of the first four principal factors of Table VI.6 as

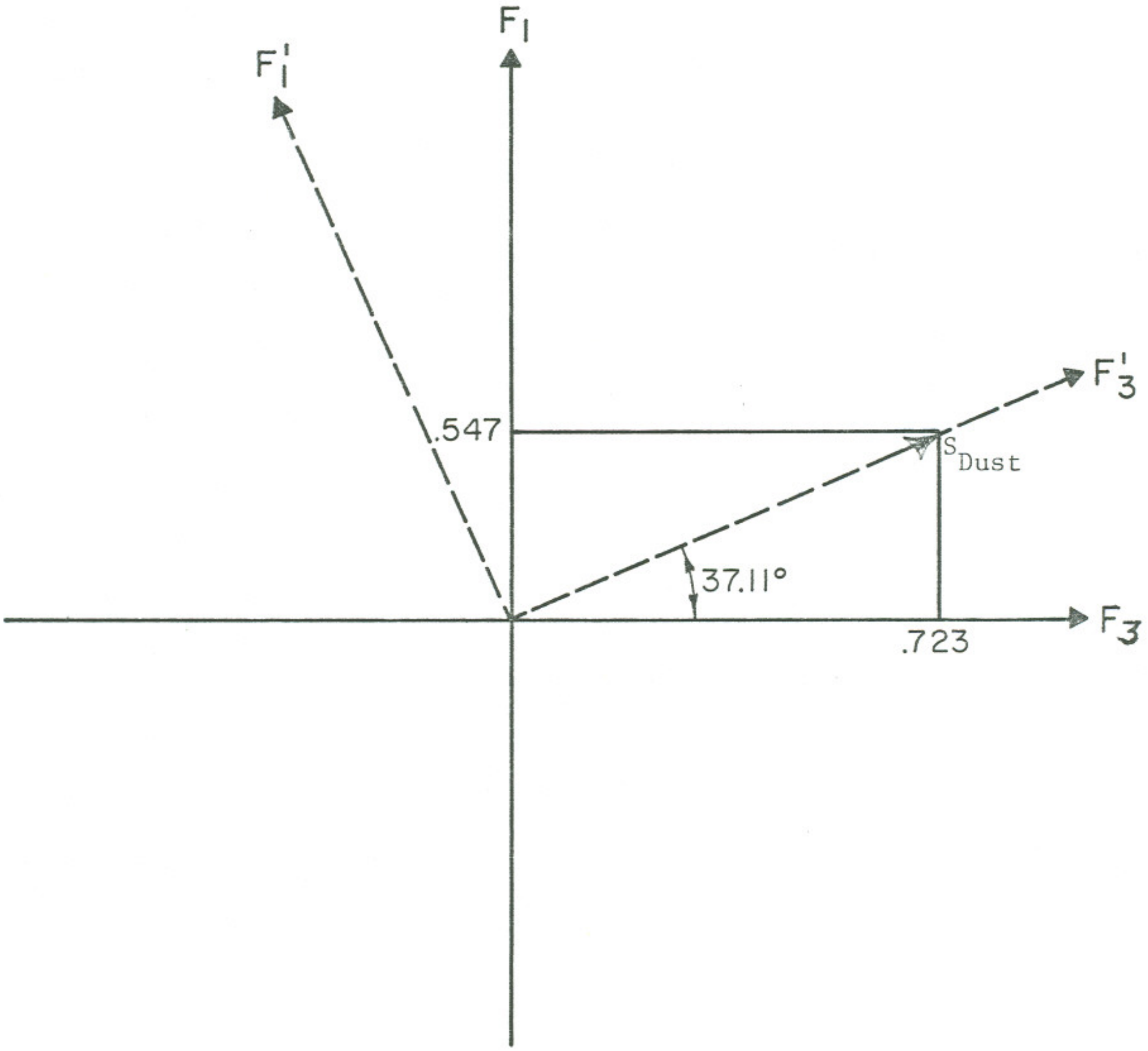
$$\tilde{S}_{Dust} = .547F_1 - .239F_2 - .723F_3 + .0619F_4$$

Only the first four factors are used because they account for more than 90% of the total observed variance.

Note that the dust factor correlates most highly with the negative of the third principal factor. The principal factor solution is rotated so that the third principal factor coincides with the dust factor. This is done by rotating the factors systematically, one at a time, with the third factor so as to reduce the factor loadings to zero. For example, factor 3 is rotated 180 degrees to change its correlation with the dust factor from -.723 to +.723. Then factors 1 and 3 are rotated by $\Theta = \tan^{-1}(.547/.723) = 37.11$ degrees. This reduces the dust factor coordinate on factor 1 to 0 (see Figure III.1). The other factors are similarily rotated. The third factor then coincides closely with the standardized street dust source. The final results are seen in Table VI.10 and discussed at length later.

The above methods are intended to reduce the d_{oj} to zero; however, since the d_{oj} are the result of a least squares fit to the standardized source, the rotated factor still does not correspond exactly with the source factor. Thus, a procedure is needed to aline the factor more precisely with the source factor deduced from the assumed source composition.

The key to development of such a procedure is to find a criterion that is satisfied only when a factor and source factor are identical. In the example above, silicon was used to obtain an estimate of σ_{Dust}. The



ROTATION OF THE PRINCIPAL AXIS SOLUTION

Figure III.1

same formula could have been used to obtain a different estimate of σ_{Dust} for each element found in street dust. If the factor was equal to a standardized street dust source, then all these estimates would be the same. In general, the closer the estimates of the source standard deviation are to being equal, the closer the factor is to the source factor. This criterion is made quantitative by requiring that the mean square deviation, or variance, of the set of estimates of the source standard deviation be minimized. For some source factor $\tilde{S}_1$, by (13A)

$$\sigma_{S_1} = \alpha_{i1} \, \sigma_{P_i} / a_{i1} \quad .$$

Let

$$h_i = a_{i1} / \sigma_{P_i} ,$$

thus

$$\sigma_{S_1} = \alpha_{i1} / h_i \quad .$$

where α_{i1} is the factor loading of element i in source factors $\tilde{S}_1$ and a_{i1} is the fraction of element i in source S_1. The following development is similar to the development of the quartimax method, (Harmon 1967, pp. 298-302).

The variance of the estimates of σ_{S_1} is

$$V = \frac{1}{n} \sum_{i=1}^{n} (\alpha_{i1}/h_i)^2 - \frac{1}{n^2} (\sum_{i=1}^{n} \alpha_{i1}/h_i)^2 \quad . \tag{17}$$

If the factors 1 and q are rotated by Θ, then

$$\alpha'_{i1} = \alpha_{i1} \cos \quad + \alpha_{iq} \sin \Theta \quad . \tag{18}$$

Multiply (17) by n^2 and use (18) to obtain

$$V(\Theta) = n \sum_{i=1}^{n} (\alpha_{i1} \cos \Theta + \alpha_{iq} \sin \Theta)^2 / h_i^{\,2} - \left[\sum (\alpha_{i1} \cos \Theta + \alpha_{iq} \sin \Theta)/h_i \right]^2 .$$

$V(\Theta)$ is minimized by finding $dV/d\Theta$ such that

$$\frac{dV}{d\Theta} = 0 \text{ and } \frac{d^2V}{d\Theta^2} > 0 .$$

In appendix C it is shown that the first condition implies:

$$\left[n \sum_i (\alpha''^{\,2}_{iq} - \alpha''^{\,2}_{i1}) - ((\sum_i \alpha''_{iq})^2 - (\sum_i \alpha''_{i1})^2) \right] \sin 2\Theta = \left[(\sum_i \alpha''_{iq}) (\sum \alpha''_{i1}) - n \sum_i \alpha''_{i1} \alpha''_{iq} \right] 2 \cos 2\Theta , \qquad (19)$$

where

$$\alpha''_{ij} = \alpha_{ij}/h_i .$$

Let

$$A = \sum_i \alpha''_{i1}, \; B = \sum \alpha''^{\,2}_{i1} ,$$

$$C = \sum_i \alpha''_{iq}, \; D = \sum_i \alpha''^{\,2}_{iq} ,$$

and

$$E = \sum_i \alpha''_{i1} \alpha''_{iq} .$$

Therefore, from (19)

$$\tan 2\Theta = \frac{2(AC - nE)}{n(D - B) - (C^2 - A^2)} .$$

If

$$T_o = 2(AC - nE),$$

and

$$B_o = n(D - B) - (C^2 - A^2) \ ,$$

then

$$\Theta = \frac{1}{2} \tan^{-1}(T_o/B_o). \tag{20}$$

The calculation of the second derivative is necessary to determine which solutions of (20) result in a minimum for $V(\Theta)$. Equation (19) can be written

$$\frac{dV}{d\Theta} = B_o \sin 2\Theta - T_o \cos 2\Theta \ .$$

From which it follows that

$$\frac{d^2V}{d\Theta^2} = 2\ T_o \sin 2\Theta - 2\ B_o \cos 2\Theta \ .$$

This last expression must be >0 for a minimum. At the turning point,

$$\cos 2\Theta = (B_o \sin 2\Theta)/T_o \ ;$$

therefore,

$$\frac{2(B_o{}^2 + T_o{}^2)}{T_o} \ \sin 2\Theta > 0 \ .$$

Since $2(B^2 + T^2)$ is always greater than zero, Θ must satisfy

$$\frac{\sin 2\Theta}{T_o} > 0 .$$

The rules deduced from this inequality for determining the quadrant of Θ are given in Table III.2.

The procedure is to rotate the factors, one at a time, with respect to the source factor until the function $V(\Theta)$ does not decrease

Table III.2

RULES TO DETERMINE Θ SO THAT III - 17 IS A MINIMUM

Algebraic Sign of				
T_o and sin 2Θ	B_o	Tan 2Θ	Resulting Quadrant of 2Θ	Range of Θ
+	+	+	I : $0^\circ < 20 < 90^\circ$	0 to 45°
+	-	-	II : $90^\circ < 20 < 180^\circ$	45° to 90°
-	-	+	III : $-180^\circ < 20 < -90^\circ$	-90 to -45
-	+	-	IV : $-90^\circ < 20 < 0^\circ$	-45 to 0°

significantly. The method is restricted to factors that are already fairly close to representing a real source. A zero factor gives $V = 0$, which is a global minimum; thus, the minimization must start near a local minimum or there is a risk of obtaining a null solution.

Further elaboration of this method is useful. Many times only one element in the source is known with any confidence, this is usually the tracer element. One possible approach to this problem would be to weight the influences of the elements in expression (17). This is done most simply by letting

$$h_i = W_i^{1/2} \; a_{i1}/\sigma_{P_i} \; .$$

The square root of the weights is used because h_i^2 appears in (17). The weights obey the usual condition

$$\sum_{i=1}^{n} W_i = 1 \; .$$

This method was not used because no nonintuitive rules for the determination of the weights could be found.

It was decided to use a variation of equation (17), instead of weights. Let α_{ij} be the factor loading for the tracer element for the source factor j, then minimize

$$V = \sum_{i=1}^{n} \left(\frac{\alpha_{ij}}{h_i} - \frac{\alpha_{Tj}}{h_T} \right)^2 . \tag{21}$$

This expression is the variance of the σ_{S_i} calculated for the other elements relative to the σ_{S_i} calculated for the tracer element. The σ_{S_i} calculated from the tracer is treated as the correct value. Every other element is compared to the tracer alone. In equation (17) the

σ_{S_i} calculated from each element is compared to the mean of all the σ_i calculated from all the elements. Thus, if one or more elements are not accurately known, these elements could bais the value of V. Expression (21) is free from this difficulty. The expression for the minimizing angle of rotation is similarly found to be

$$\text{Tan } 2\Theta = \frac{2(F_1 - D_1 - E_1)}{A_1 + B_1 + C_1} , \qquad (22)$$

where

$$A_1 = \sum_i (\alpha_{iq}^{''2} - \alpha_{i1}^{''2}),\ B = n(\alpha_{Tq}^{''2} - \alpha_{T1}^{''2}) ,$$

$$C_1 = 2\sum_i (\alpha_{i1}^{''}\alpha_{T1}^{''} - \alpha_{iq}^{''}\alpha_{Tq}^{''}),\ D = \sum_i \alpha_{i1}^{''}\alpha_{iq}^{''} ,$$

$$E_1 = n\alpha_{T1}^{''}\alpha_{Tq}^{''},\ \text{and}\ F_1 = \sum_i (\alpha_{i1}^{''}\alpha_{Tq}^{''} + \alpha_{Ti}^{''}\alpha_{iq}^{''}) .$$

If

$$T_o' = 2(F_1 - D_1 - E_1) \quad \text{and}$$

$$B_o' = A_1 + B_1 + C_1 ,$$

then the rules for determining Θ are the same as given in Table III.2. This is the algorithm actually used in the calculations reported in this dissertation.

The factor obtained by the above rotations is as nearly identical to the source factor as is possible given the constraints of the problem. The next step is to use equation (13) to convert the factor loadings to the elemental composition of the source. Note that only the amount of one element in the source was needed to carry out the above analysis. Thus, the knowledge of the mass fraction of one element in a source and its intercorrelations can be used to deduce the remaining elemental composition of the source. This is one of the most surprising and useful results of this model.

Finally, the procedures detailed above are applied to each suspected source of aerosol. In this way, a new source matrix is generated. This new source matrix is compatible with the observed variances and correlations of the elements since it is derived from the principal factor solution. A chemical element balance is carried out on the aerosol mean element concentrations with this new source matrix. The end result is the second order aerosol model that was sought.

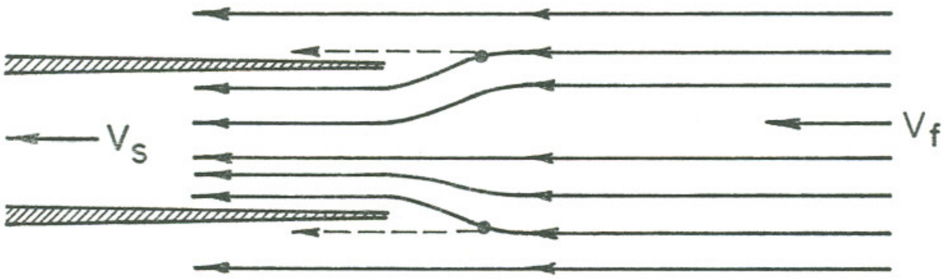
CHAPTER IV

EXPERIMENTAL METHODS OF AEROSOL SAMPLING

INTRODUCTION

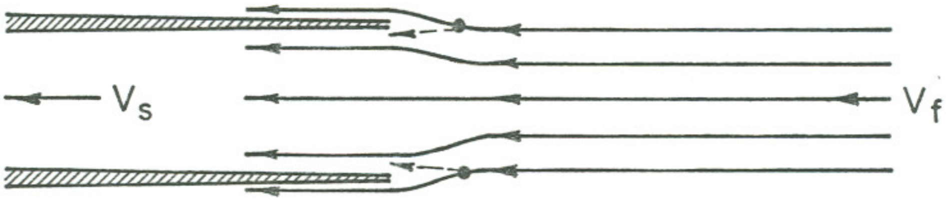
With the increasing interest in aerosols in the last twenty years has come the realization of the difficulties of obtaining representive samples of ambient aerosols (Luna, Church and Shreve, 1971, and Lee, Caldwell and Morgan, 1972). Fuchs (1975) presents an interesting recent review of the subject. The difficulties are many, e.g., long, thin sampling tubes may lose small particles by diffusion to the walls; or the pumps and sampling apparatus may introduce contamination. These problems are usually quickly solved once they are discovered. However, the major difficulty in good ambient aerosol sampling practice is anisokinetic sampling.

Anisokinetic sampling conditions prevail if the velocity of the fluid in the sampling tube is not equal to the velocity of the fluid outside the tube. The result is nonuniform flow of the fluid near the sampling inlet. Particles with large momentum cannot follow the streamlines of the flow if they bend too sharply. This gives rise to either overestimation or underestimation of the concentration of the large particles. The effect is illustrated in Figure IV.1, which is adapted from Fuchs (1964). This phenomenon has been studied experimentally by Watson (1954) and theoretically by Davies (1968) and Agarawal (1975).



(a) $V_s > V_f$

Total Mass Underestimated



(b) $V_s < V_f$

Total Mass Overestimated

ANISOKINETIC SAMPLING ERRORS

Figure IV.1

The sampling apparatus used in collecting the aerosol samples for this study was designed to allow several instruments to simultaneously sample the same aerosol isokinetically. This was accomplished by sampling inside an isokinetic manifold, which is described in detail below. The aerosol collection instruments included a total mass filter, a Lundgren inertial impactor, and an Anderson inertial impactor. However, this dissertation is concerned only with the samples collected on the total mass filters.

SAMPLING INSTRUMENTATION AND TECHNIQUES

A total of eighteen experiments were run during August and September of 1975. The first four were test runs. All but the initial two runs, which were performed at the Oregon Graduate Center, were carried out on the roof of the Equitable Savings and Loan Building in downtown Portland, Oregon. This building is five stories high. A list of the dates, times and average wind conditions of the fifteen experiments used in this study is given in Table IV.1. The weather was uniformly warm and dry, except for occasional morning fog.

The aerosol samples were collected inside an isokinetic sampling manifold. It was originally desired to have the ability to sample the same aerosol isokinetically with several different instruments. The isokinetic manifold was designed to provide a constant internal air velocity. Allowance was made for three sampling tubes to be placed inside the manifold. The sizes and flow rates through these sampling tubes were chosen so that isokinetic sampling conditions were obtained

Table IV.1

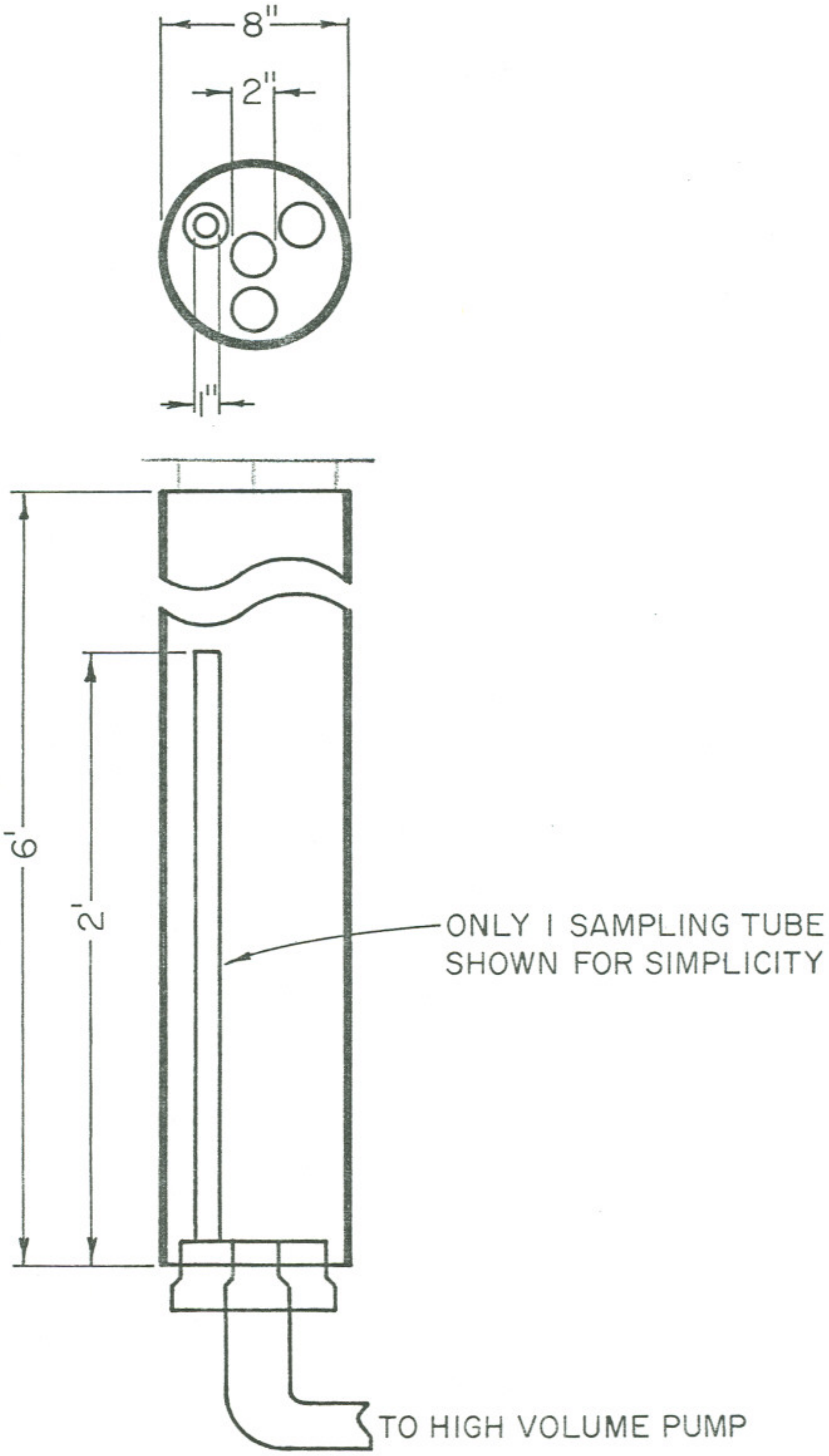
Meteorological Conditions During Periods of Sample Collection

Experiment No.	Dates (Sept.) 1975	Time (PST)	Average Wind		Resultant Wind		% Wind from Quadrant			
			Speed (MPH)	Direction (°)	Speed (MPH)	Direction	0-90	90-180	180-270	270-360
5	2 - 3	10:45 - 10:45	8.63	325	8.5	327				100
6	4 - 5	12:15 - 19:15	6.85	352	5.7	345	46			54
7	8 - 9	9:50 - 9:30	7.93	326	7.7	326				100
8	9 - 10	10:00 - 11:00	10.04	320	10.0	319				100
9	10 - 11	12:00 - 13:00	8.50	323	7.64	322	4			96
10	12 - 13	10:15 - 10:00	5.39	338	3.73	342	25			75
11	13 - 14	11:00 - 10:20	4.19	288	3.12	322	8	17		75
12	14 - 15	11:00 - 12:50	5.32	322	4.99	328	4	4		92
13	15 - 16	13:30 - 13:00	5.15	331	4.98	332	8		4	88
14	16 - 17	13:50 - 11:00	5.91	312	5.54	315	5	5		90
14A	17 - 18	11:25 - 13:00	8.49	329	6.97	328	12			88
14B	18 - 19	13:15 - 19:45	7.29	7	4.48	22	48			52
15	23 - 24	10:30 - 10:25	6.03	320	5.45	327		4		96
16	24 - 25	11:00 - 9:40	5.10	279	4.14	321		21	4	75
16A	25 - 26	10:20 - 10:20	6.70	319	6.59	320				100

inside the manifold. Note that no attempt was made to sample the ambient aerosol isokinetically.

The manifold consisted of a six foot length of eight inch diameter polyvinyl chloride plastic pipe, shown schematically in Figure IV.2. It was held vertically by a triangle of two by four wooden struts. Five cm above the top of the tube, an aluminum plate was placed to keep out rain. Directly over the mouth of the tube a plastic mesh was mounted to remove insects and other large debris. A high volume air sampler pump attached to the center port on the bottom of the tube provided the general air movement through the system. Three sampling ports were arranged symmetrically about the axis of the tube. Varying diameters of plastic pipe could be attached inside the ports so as to match the sampling velocity of the port to the general velocity of the air inside the manifold.

The total mass filters were 47 mm, .45 micron pore size Millipore filters. These are cellulose acetate, membrane type filters that have levels of trace elements below the minimum detectable limits of the analysis technique used in this study. Only calcium is present in blank filters in measureable amounts. This background of calcium is reduced to nil by washing the filters in water. The filters were placed in an open faced Gellman filter holder attached to the sampling port by large diameter plastic tubing and secured by hose clamps. The sampling tube inside the manifold was a 1.2 inch inside diameter, plastic pipe. The nominal flow rate was 18 l/min. at standard temperature and pressure. All flows were measured with a



THE ISOKINETIC SAMPLING MANIFOLD

Figure IV.2

rotameter which had been calibrated against a wet test meter as described in Brenchley, Turley and Yarmac (1973).

All filters were equilibrated inside a 50% relative humidity chamber which contained a five place Mettler balance. In addition to tare weights, weights of two control filters that remained in the box were taken at each weighing. After sample collection, the filters were charge neutralized with an α-particle emitting source. They were then returned to the 50% humidity box for at least eighteen hours. The second weight and the control weights were taken and the change in mass corrected by the average change in the control filters. This was done to correct for systematic changes in the weighing box conditions that gave rise to weight changes on the order of 50 micrograms per filter per day. A study of twelve weights similarly obtained showed no bias errors and a standard error due to weighing and handling of 50 micrograms.

ERROR ANALYSIS OF THE GRAVIMETRIC DATA

The purpose of the sample collection was to obtain the total aerosol mass and the concentrations of various elements in the aerosol. The usual units are micrograms per cubic meter. The basic measurements were the change in mass of the filter, the flow through the filter and the duration of the experiment; all these were subject to error. Quantitatively, the errors can be estimated as follows. Let

$$M = \text{Total mass loading}$$

$$= \Delta M/\Delta V = \Delta M/(FT),$$

where

ΔM = mass increase (μg),

ΔV = volume of the air sample (m^3) ,

F = average flow rate (m^3/min) ,

and

T = duration of the flow (min).

Let E_x be the error in the measurement of x, then

$$M + E_M = \frac{\Delta M + E_{\Delta M}}{(F + E_F)(T + E_T)} \quad .$$

Ignoring second order terms,

$$E_M = \frac{1}{FT}\left(E_{\Delta M} - \Delta M\frac{E_F}{F} - \Delta M\frac{E_T}{T}\right) .$$

The standard error is then

$$\sigma_M = \frac{1}{FT}\left(\sigma^2_{\Delta M} + \left(\frac{\Delta M}{F}\right)^2 \sigma^2_F + \left(\frac{\Delta M}{T}\right)^2 \sigma^2_T\right)^{1/2} \quad , \qquad (1)$$

where σ_x is the standard error of x. Typical values for the variables are

$F = 18\ l/m = 1.8 \times 10^{-2}\ m^3/min$,

$T = 24$ hr. $= 1440$ min.,

$\Delta M = 2.5\ mg = 2500\ \mu g$,

and

$\Delta M/\Delta V = 96\ \mu g/m^3$.

The errors in measurement are estimated as follows:

$\sigma_{\Delta M} = 50\ \mu g$,

$\sigma_F = .5\ l/m = 5 \times 10^{-4}\ m^3/min$,

and

$$\sigma_T = 2 \text{ min} .$$

Thus, the terms in parenthesis in equation (1) are

$$\sigma_{\Delta M}^2 = 2500,$$

$${\frac{\Delta M \sigma_F}{F}}^{2} = 4823 ,$$

$${\frac{\Delta M \sigma_T}{T}}^{2} = 12 ,$$

and

$$\sigma_M = 3.3 \ \mu g/m^3 = 3.4\% .$$

The error in time is negligible while the flow error is two thirds of the total error. Similar reasoning can be used to determine the error bars for the elemental concentrations. All that is necessary is to interpret $\sigma_{\Delta M}$ as instrumental error in the X-ray fluorescence determination of the elemental concentrations. The results are given in Chapter V.

CHAPTER V

X-RAY FLUORESCENCE ANALYSIS OF AMBIENT AEROSOLS

INTRODUCTION

The basic physical principle behind X-ray fluorescence analysis, XRF, was discovered by Moseley in 1913. Moseley observed that, when suitably excited, every element produces X-rays of a characteristic energy. It is now known that these X-rays are the result of electrons falling into vacancies created in the inner shells of the atom by the exciting radiation. If the X-ray is the result of an electron transition to the K, or lowest energy shell, it is called a K X-ray; if the transition is to an L shell it is called an L X-ray, and so on. Thus, every element has a characteristic X-ray spectrum, just as it has a specific optical spectrum. This X-ray spectrum has fewer lines than the optical spectrum and can be used in the same way to identify and quantitate the elements in a sample. It is only necessary to count how many X-rays of each energy are produced by the excited sample.

X-ray fluorescence has become a standard method of analyzing samples of aerosols collected on filters. Birks and Gilfrich (1976) review X-ray fluorescence work in general, including applications to environmental monitoring. There are several reasons for the widespread use of this method of instrumental analysis. The technique requires no elaborate sample preparation, which is important in air pollution work because of the large number of samples. Also, X-ray analysis is nondestructive, allowing for the further analysis of the samples by other techniques. The analysis time for fifteen to twenty elements is usually less than a thousand seconds, an advantage over wet chemical or spectroscopic methods. Finally, X-ray analysis offers good sensitivity, around 0.01% by weight, for many elements of interest.

X-RAY FLUORESCENCE TECHNIQUES

The equipment used in this study was purchased from EDAX International, Inc., now a subsidiary of Phillips. The exciting radiation is the characteristic and bremsstrahlung radiation produced by a gold anode, low voltage X-ray tube. A lithium drifted silicon, Si(Li), X-ray detector is used. The detector is separated from the sample chamber by a 0.3 mil beryllium window. The irradiation chamber is evacuated to eliminate air absorption of the soft X-rays produced by the lighter elements. The pulses from the detector are processed electronically and fed into a multichannel analyzer. This analyzer is interfaced to a Data General Nova 1210 minicomputer which controls the entire system. The full width at half maximum, FWHM, of this system for manganese K_α X-rays at 5.89 Kev is 181.5 electron volts.

The aerosol loaded filters were cut in half and mounted between 0.5 mil mylar film in standard 35 mm slide mounts. The slide was then analyzed for 400 seconds. The X-ray tube voltage was set at 22.0 KV and 256 mA current. The number of counts in each channel of the multichannel analyzer was punched on to paper tape by the minicomputer. This paper tape was then read into the Prime 300 computer system at the Center and the integrated intensities of the peaks in the spectrum were calculated.

CALIBRATION OF THE X-RAY SPECTROMETER

It is shown in Bertin (1975), p. 623, that for thin, homogeneous samples of thickness t for a given element i, the fluorescent intensity, I_i, can be expressed as

$$I_i = \frac{T_i P_i I_o}{\bar{\mu} P} [1 - \exp(- \bar{\mu} p t)] ,$$

where

I_o = intensity of the incident radiation,

T_i = excitation constant of element i,

P_i = density of element i in the layer,

P = density of the sample,

$\bar{\mu} = \mu_p \csc \phi + \mu_F \csc \psi$,

μ_p = mass absorption coefficient of the sample for incident radiation,

μ_F = mass absorption coefficient of the sample for fluorescent radiation,

and

ϕ and ψ = angles with the normal of the incident and fluorescent radiation.

If t is small enough to allow the expoential approximation,

$$\bar{\mu}_p t = 1 - \exp\left(-\bar{\mu}_p t\right) , \tag{2}$$

then

$$\begin{aligned} I_i &= \frac{T_i P_i I_o}{\bar{\mu}_p} \bar{\mu}_p t \\ &= T_i I_o P_i t , \\ &= T_i I_o L_i , \end{aligned}$$

where (3)

L_i = loading of the element in the sample with units of mass/area.

Equation (3) shows that for thin samples the observed count rate is simply proportional to the loading of the element.

Commercially available thin film standards deposited on mylar were used to calibrate the system. The standards were analyzed through 0.5 mil mylar film in the same manner as the samples; the analysis time was nominally 40 seconds. Table V.1 lists the standards used, their loadings and sensitivities. The sensitivities of those elements for which standards are not available are found by interpolation on a graph of the sensitivities of the standards vs. atomic number. This graph is seen in Figure V.1. The plot is smooth except for Al and Si. The M line of the gold X-ray tube is placed just above the absorption edges of Al and Si. This is the reason for the enhanced sensitivity to these elements.

The sensitivities calculated for Al and Si are in error because the standards for these elements do not obey the thin film criterion

Table V.1

THIN FILM CALIBRATION STANDARDS USED AND MINIMUM DETECTABLE LIMITS OF ANALYSIS

Element Line	Mass Loading ($\mu g/cm^2$)	Sensitivity (counts/sec) ($\mu g/cm^2$)	Full Width at Half Maximum (ev)	Minimum Detectable Limits Mass Loading (ng/cm^2)	Minimum Detectable Limits Aerosol * Concentration (ng/m^3)
Al Kα	122	2.75	144	294	118
Si Kα	61.8	10.00	147	135	54
Cl Kα	51.4	8.81	156	90	36
K Kα	56.6	12.57	160	74	30
Cu Kα	42.6	14.24	164	72	29
V Kα	53	15.91	174	62	25
Mn Kα	144	18.31	181	54	22
Fe Kα	118	18.66	185	49	20
Cu Kα	68	19.04	198	45	18
Zn Kα	63	19.36	206	43	17
Pb Lα	184	1.72	220	509	204

* Assuming 10 cm^2 collection area and 25 m^3 sample volume.

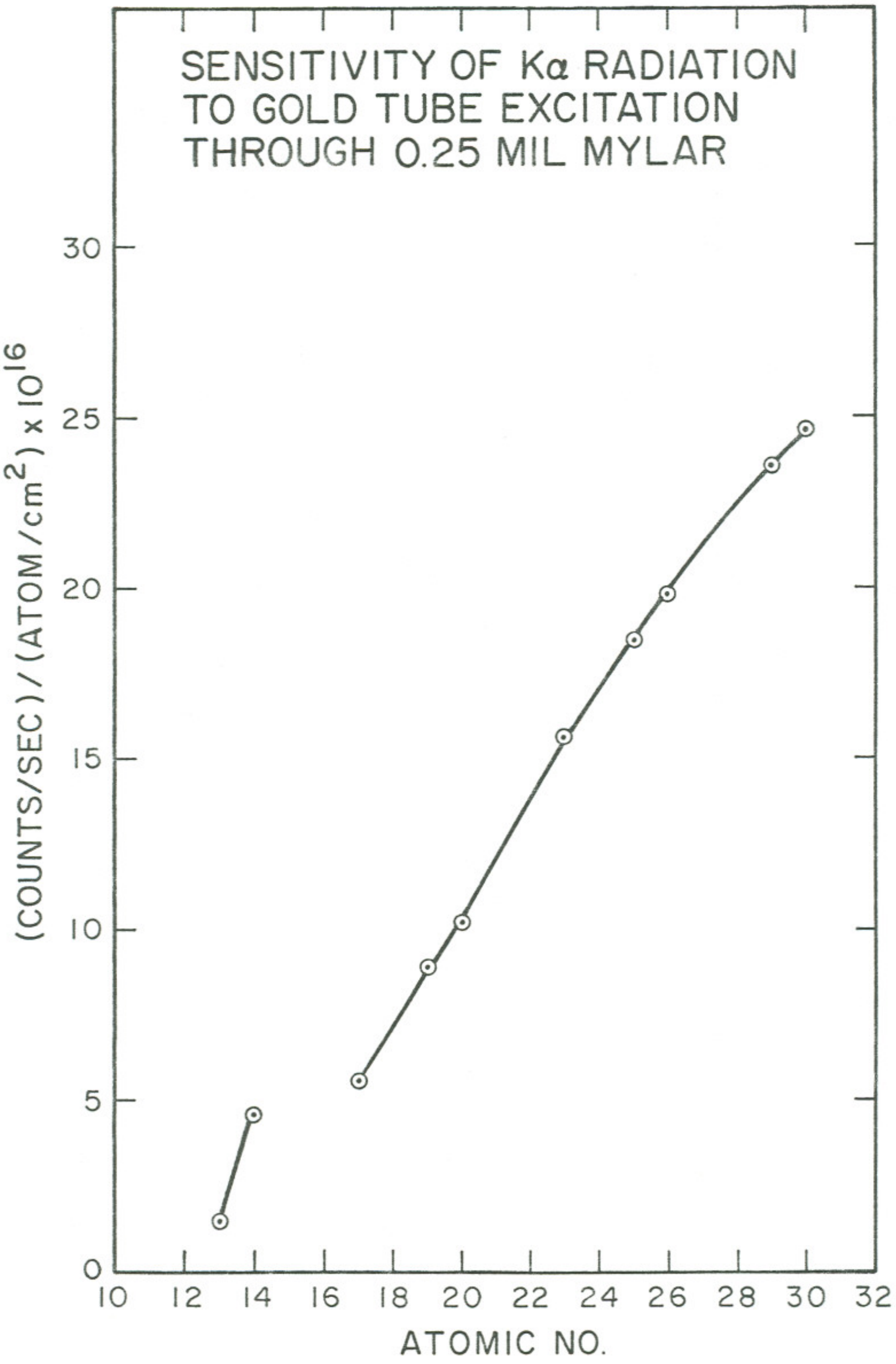

SENSITIVITY OF Kα RADIATION TO GOLD TUBE EXCITATION THROUGH 0.25 MIL MYLAR
(COUNTS/SEC) / (ATOM/cm²) x 10¹⁶
0
5
10
15
20
25
30
10
12
14
16
18
20
22
24
26
28
30
32
ATOMIC NO.

Figure V.1

(2). The exciting radiation in this case is the Au M line. The mass absorption coefficients of Al for Al K and Au M radiation are 386 and 2033 cm^2/g, respectively. The angles Θ and ψ for the system are approximately 45°, and the loading of Al is 122 $\mu\mathrm{g}/\mathrm{cm}^2$. Using these values,

$$\bar{\mu}_p t = (386 + 2033)(\csc 45°)(122 \times 10^{-6})$$
$$= .417,$$

but

$$1-\exp(-.417) = .341 \ .$$

Thus, the approximation (2) is not valid. Similar calculations show that the same is true of the Si standard. This problem is overshadowed, however, by the particle size correction for Al and Si, which is taken up in detail later.

Of course, the sensitivities for the elements are a function of the X-ray tube voltage and current. The operating conditions of the X-ray tube were 22.0 KV and 256 mA. These conditions were arrived at by determining the minimum detectable limits of the elements in a typical aerosol sample as a function of the tube voltage. The tube current is set as high as possible while keeping the total count rate below 5000 counts/sec; the electronics of the system do not respond linearly at higher count rates. The above conditions give the maximum sensitivity to the higher atomic number elements without degrading the signal to noise ratios of the lower atomic number elements.

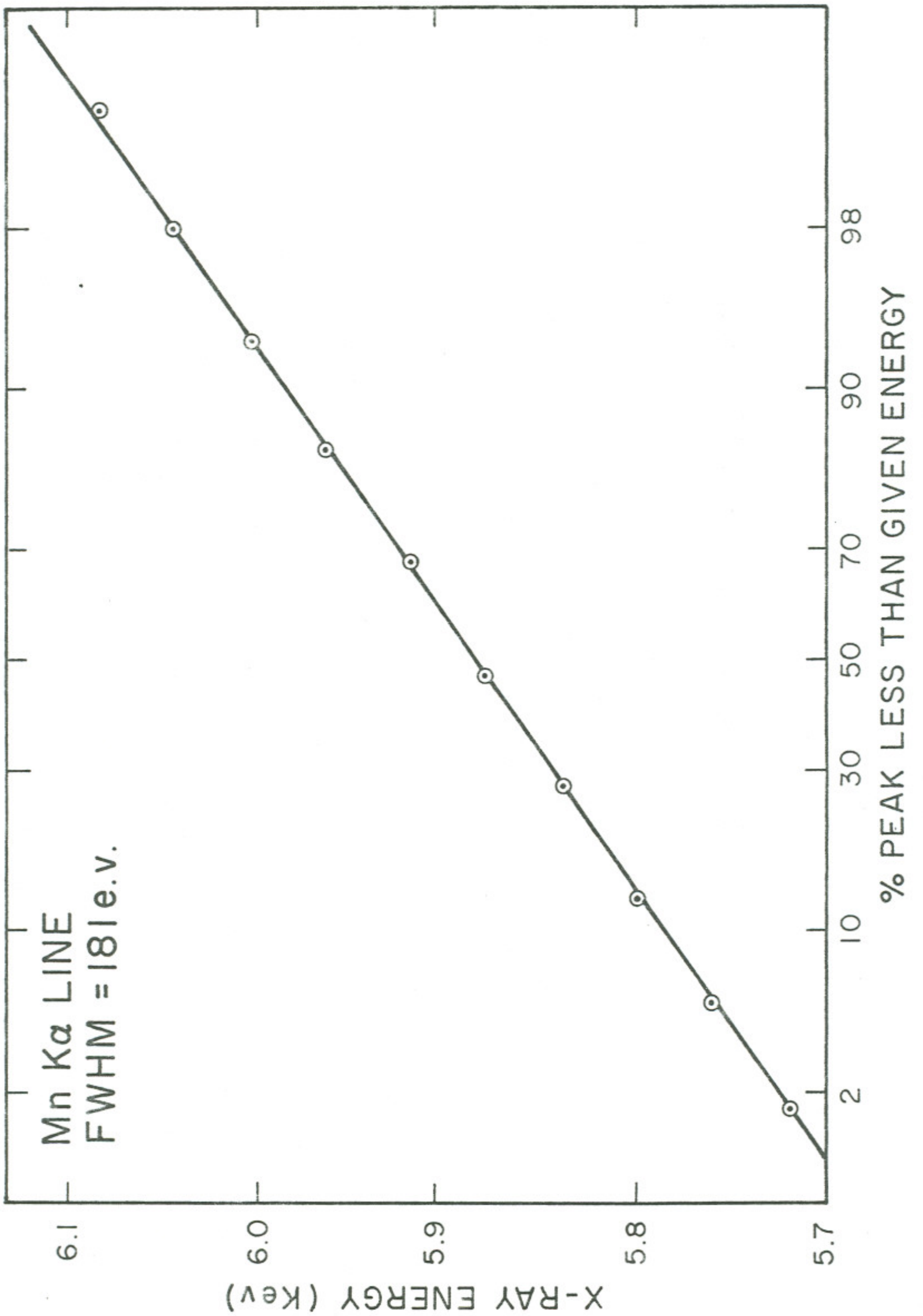
The full width at half maximum, FWHM, was also measured experimentally for some of the standards. The results are given in Table V.1.

This was done by plotting the cumulative area of the peak on probability paper, as in Figure V.2. A gaussian peak will give a straight line on this type of graph. 88% of the area of the peak is below one half FWHM above the mean; 12% of the area is below one half FWHM below the mean. The FWHM is the difference of the energies corresponding to these two points. One can theoretically relate the energy of the peak, E, to the FWHM of the Mn Kα line, R, by the equation

$$\mathrm{FWHM} = [R^2 + 2.735(E - 5894)]^{1/2} \ . \qquad (4)$$

This equation is taken from Russ (1972) and adequately describes the experimental results, except for lead and zinc. The peak widths for zinc and lead differ significantly from the predictions of equation (4), and the lead peak is not exactly gaussian. For these elements the best experimentally determined gaussian peak approximations were used.

The minimum detectable limits of the elements were determined from a spectrum of a blank filter. The number of counts in the channels corresponding to the element were summed; the standard error of this sum is its square root. The minimum detectable limit was taken to be three times the standard error. The minimum detectable element loadings are then found by dividing the minimum detectable count by the respective sensitivities of the elements. The results are given in Table V.1.



ACCUMULATIVE AREA PLOT OF Mn Kα PEAK
Figure V.2

INTEGRATION OF THE X-RAY SPECTRA

It has been recognized for several years that a major difficulty in X-ray fluorescence analysis using the Si(Li) detector is in the mathematical integration of the spectra (Cooper, 1973). The main problem is the overlap of the peaks in the spectrum. In analyzing air pollution samples the problem is at its worst because of the large number of elements present and their extremely low and variable concentrations. A further difficulty results from the presence of background due to scattered exciting radiation; this background must somehow be estimated and eliminated. A complete review of the subject has been written by Statham, (1976).

For air pollution work the usual methods used to integrate the spectra are linear background subtraction and linear least squares curve deconvolution based on the assumption of gaussian peak shapes. Statham shows that for the case of a large peak near a small one errors of about 10% in the smaller peak would be expected using these methods. Unfortunately, this case is very common due to the presence of $K\alpha/K\beta$ interferences. For example, the K $K\beta$ peak is only 101 ev below the Ca $K\alpha$ peak. The $K\alpha$ lines of Ca and K are only 378 ev apart. This gives rise to a situation not at all well suited to the usual deconvolution methods. Other $K\alpha/K\beta$ interferences are even worse; the Ti $K\beta$ and V $K\alpha$ peaks are separated by only 18 ev. In such cases, which are quite common, the only recourse is to deduce from the $K\alpha$ peak the size of the $K\beta$ peak and subtract it. The $K\alpha/K\beta$ intensity ratios can be measured from standards or taken from published data; see Salem, Falconer and Winchell (1972), for instance.

The problem of background subtraction is not as serious for air pollution filter samples as for other types of samples. This is because the backgrounds are slowly varying and the presence of the sample does not much alter the scattered background. All that is needed is to subtract a suitably normalized spectrum of a blank filter to remove background from parts of the spectrum that are not flat enough for ordinary linear interpolation of the background.

Statham (1976) introduces a method called iterative stripping which is the basis for the software developed to process the spectra for this study. The stripping consists of estimating the peak area, generating a peak of the proper width of that area at the right location and subtracting it from the spectrum. Two variations of this algorithm were incorporated in the program written to integrate the spectra. Table V.2. gives the method used for each element. In one case two interfering peaks are jointly stripped. This is the case with Al and Si and K and Ca. In the other case stripping is done on a single peak only. The method used to estimate the peak area is designed to minimize errors due to inaccuracies in the model gaussian function. It is called the "top hat" method and consists of estimating the area of the peak by subtracting the average counts of the tials of the peak from the counts in each channel of the center of the peak. The sum of the remaining counts in the center of the peak is the estimate of the peak area. The process terminates when the amount of peak stripped is equal to the standard error of the peak plus background. Table V.3

Table V.2

METHODS OF X-RAY INTENSITY PEAK INTEGRATION AND MANIPULATION

Method Element	Iterative Stripping	Background Subtraction	Kβ Peak Subtraction	Escape Peak Subtraction
Al	yes, with Si	yes, norm. at 2.0 Kev	no	no
Si	yes, with Al	yes, norm. at 2.0 Kev	no	no
Cl	yes, with Cl Kβ	no	no	no
K	yes, with Ca Kα	yes, norm. at 3.1 Kev	yes	no
Ca	yes, with K Kα	yes, norm. at 3.1 Kev	no	no
Ti	yes, alone	no	yes	no
V	yes, alone	no	yes	no
Cr	yes, alone	no	yes	no
Mn	yes, alone	no	yes	no
Fe	yes, alone	no	yes	yes
Ni	yes, alone	no	no	no
Cu	yes, alone	no	no	no
Zn	yes, alone	no	no	no
Pb	yes, alone	yes, norm. at 10.2 Kev	no	no

gives a typical output of the program which integrates the spectrum. In the case of the K, Ca integration the K Kβ peak was subtracted at each step of the iterative stripping. Otherwise the Kβ peak was stripped after the Kα peak had been totally integrated. The background subtraction was done by normalizing the blank spectrum to the average of several channels. Just where to normalize and how many channels to use was determined empirically.

For iron it was necessary to subtract the iron escape peak. The escape peak is an anomalous peak caused by scattering inside the detector. It occurs 1.74 Kev below the main peak because 1.74 Kev is the energy of the Si X-ray generated by the iron X-ray. The iron escape peak is therefore at 4.66 Kev, which is underneath the Ti peak. The ratio of the Fe K to the Fe escape peak was measured to be 3.59×10^{-3}. Typical Fe loadings in our samples would give Ti values of about 5% higher than the average observed Ti values.

ALUMINUM AND SILICON VALUES: PARTICLE SIZE EFFECTS

The analysis of light metals by X-ray induced X-ray fluorescence is considerably complicated by the absorption of the inducing and the fluorescent radiation by the material itself. It is not uncommon for the fluorescent radiation to be one half to one quarter less than what it would be given no such effect. Specifically, in this study particle size effects are of great importance because of the large amount of street dust in the aerosol, most of which is in large particles. The effect of this bias error on the factor analysis, however, is probably

Table V.3

PEAK INTEGRATION PROGRAM

Total Mass Load in Micrograms: 2500 Total Sampled Volume in M3: 24.11

Counts	Std. Dev.	Peak/Background	Loading	Error	Percent
3888	196.8	0.112	1.215	0.061	1.172
43656	313.5	0.799	4.364	0.031	4.208
1928	162.0	0.079	0.206	0.017	0.199
11044	217.7	0.304	0.765	0.015	0.738
37872	285.1	0.873	2.296	0.017	2.215
119772	392.7	3.479	5.653	0.019	5.452
4616	202.2	0.127	0.264	0.012	0.255
669	184.5	0.020	0.037	0.010	0.035
2898	195.0	0.082	0.149	0.010	0.144
6019	202.8	0.172	0.285	0.010	0.275
1732	160.9	0.072	0.081	0.008	0.078
1169	172.9	0.041	0.055	0.008	0.053
7724	189.0	0.276	0.347	0.008	0.335
2448	170.7	0.092	1.238	0.086	1.194

negligible. Assuming that the particle size correction factor is a constant, f, then it will cancel out of the normalized factor equations, i.e.,

$$\tilde{x} = \frac{fx - f\mu_x}{f\sigma_x} = \frac{x - \mu_x}{\sigma_x} \quad .$$

The assumption that the particle size correction is a constant is justified because the composition of the street dust is obviously not varying rapidly. Also, the size distribution of the entrained dust is a function of meteorological conditions and these were nearly constant during the sampling period. Thus, the particle size correction is important in determining the final element balance, but is of little consequence to the factor analysis.

It is assumed that the concentrations of Al and Si obtained by X-ray analysis in this study are low by a factor of three. This correction factor was chosen because it gives Si and Al concentrations in street dust samples and ambient aerosol samples that agree with the values observed by other investigators. The theoretical and experimental details are given below; however, no definitive determination of the particle size correction factor was accomplished during this study. For this reason the absolute values of the concentrations of Al and Si are possibly subject to a large bias error.

Al and Si are essentially monochromatically excited by the gold M line; thus, it is possible to calculate a theoretical particle size correction. This approach is described in Hunter and Rhodes (1972) and Rhodes and Hunter (1972). It is shown that for a monolayer of particles of average mass thickness $\bar{m}(g/cm^2)$

$$I_P = I_{thin}[(\mu_P + \mu_F)\bar{m}]^{-1}(1 - \exp[-(\mu_P + \mu_F)\bar{m}]), \quad (5)$$

where

I_P = intensity of fluorescent radiation from the particle,

I_{thin} = intensity of fluorescent radiation from a thin film,

μ_P = mass absorption coefficient of the particle for incident radiation,

and

μ_F = mass absorption coefficient of the particle for fluorescent radiation.

Therefore, the correction factor is

$$\frac{I_{thin}}{I_P} = \frac{(\mu_P + \mu_F)\bar{m}}{1 - \exp[-(\mu_P + \mu_F)\bar{m}]} \, . \quad (6)$$

It is assumed that the large particles are derived from dust with an average composition of major elements as follows:

Si - 28%
Al - 6.7%
Ca - 4.2%
Fe - 3.9%
O - 50%
other - 7.2%

This composition does not match that given later for street dust. Street dust contains nonmineral material; however, it is the mineral particles that are of interest in calculating the particle size effect. The mass absorption coefficients for Al K, Si K and Au M X-rays are read from tables and the weighted sum calculated. The value of $(\mu_P + \mu_F)$ for Al and Si is found to be close to 2000 cm^2/g. About one half of this number is due to the absorption of the Au M radiation.

The nature of the aerosol is such that the large particles are not uniformly distributed with respect to mass but have an approximately lognormal mass distribution. The effect this has on the particle size correction is surprisingly small. Dzubay and Nelson (1974) show that for lognormal mass distributions the particle size correction calculated from the mass mean was almost identical to that calculated exactly. Lundgren and Paulus (1975) report mean mass aerodynamic diameters for the large particle mode of 25 to 60 microns. A value of 30 microns is used for the following calculations. The mean mass thickness is then 15×10^{-6} cm^2/g since the aerodynamic diameter is already normalized to unit density. Using this value of $\bar{m}$, a particle size correction factor of three is obtained from equation (6). This is the theoretical justification for the correction factor assumed in this study. The next section contains the experimental verification.

A number of samples of street dust were taken during 1974 from various sections of Portland. In addition, samples of representative soils of the area were obtained from the U.S. Department of Agriculture Soil Conservation Office in Hillsboro. All soil and street dust samples were passed through a 44 micron sieve and mechanically puffed onto membrane filters similar to those used to collect aerosol samples. The dust aerosol was allowed to settle for fifteen seconds before collection on the filter. These dust samples and ambient aerosol samples seemed to have the same large particle size distribution as determined by microscopic observation. No quantitative data is available to support this assertion. The dust loaded filters were then subjected to exactly the same X-ray analysis as the aerosol loaded filters. Three samples of street dust, one each from an industrial, a commercial, and a residential area of Portland were analyzed. A sample of Willamette silt loam, typical of soils in the area, was similarly analyzed. These four analyses and their average are found in Table V.4 the correction factor of three was used to obtain the Al and Si numbers. The concentrations found in Table V.4 are reasonable when compared to other studies, see Hansford, et al. (1971). The average values will be used in the sequel as representative of dust in the Portland aerosol. Note that the average is weighted three quarters street dust and one quarter soil dust.

The last possible source of error left to discuss is the absorption of X-rays by the filter. This is known to be of importance for fiber type filters, such as Whatman type 41. In the case of the .45 micron pore size membrane filters used in this study the penetration of the filter by particles seems to be negligible. Thus, the absorption of the X-rays by the filter is ignored. Adams and Van Grieken (1975) in a discussion of the magnitude of absorptive filter effects also come to this conclusion for .45 micron membrane filters.

The error analysis for the total mass determinations has already been done. It remains to determine the error in the elemental mass loadings. The error in the loadings has three sources: counting error, spectrum manipulation error, and integration error. The counting error is due to statistical fluctuation in the X-ray spectrum and is equal to the square root of the peak plus background. Except

Table V.4

COMPOSITION OF SOIL AND STREET DUSTS

(weight percent)

Element	Industrial	Residential	Commercial	Willamette Silt Loam	Average Dust
Al	8.43	7.02	4.98	9.72	7.54
Si	17.5	20.8	17.1	23.7	19.9
K	0.553	0.601	0.611	1.38	0.786
Ca	1.69	2.20	2.10	0.348	1.59
Ti	0.700	0.618	0.544	0.718	0.645
Mn	0.391	0.026	0.038	0.066	0.131
Fe	7.29	5.63	5.22	4.33	5.62
Cu			0.021		
Zn	0.198		0.078		.030
Pb	0.204	0.325	0.587		.279

for Ca, Fe and Si, in our spectra the peaks are small compared to the background and since the background does not vary much the counting error is always the same, about 200 counts. The major manipulative error is the background subtraction. For elements for which this is done the increase in variance is a factor of two, since the variance of a difference is the sum of the variances. The iterative stripping technique of integration introduces error also. The integration error is approximately equal to the counting error. This assumption is the result of a simplified error analysis of Statham's integration procedure. Basically, the method consists of a linear background subtraction and a series of peak estimations. Thus, the variance due to this process is the square root of the peak plus background; but this is just the total counting error.

Table V.5 is a summary of the error analysis, assuming an error of 2.8% due to errors in sample collection. The elements fall into four groups: 3% error, Si, Fe and Ca; 5% error, K, Ti, Mn and Zn; 10% error, Al, Cl, Cr, Ni and Cu; and 35% error for V. Of course, most of the percentage errors involved decrease with increasing number of counts, and it must be remembered that the Al and Si values are possibly subject to a large systematic error, because of particle size effects.

Table V.5

ERROR ANALYSIS SUMMARY

Element	Average Counts	Peak Background	Counting Error	Background Sub. Error	% Counting and Manip. Error	% Total Error
Al	5100	.13	213	213	5.9	8.8
Si	40000	.8	300	220	0.93	3.1
Cl	2000	.08	164	0	8.2	12
K	12000	.37	210	210	2.5	4.5
Ca	30000	.80	260	194	1.1	3.2
Ti	5000	.14	202		4.0	6.3
V	700	.02	185		26	37
Cr	2000	.06	190		9.5	14
Mn	6000	.17	200		3.3	5.4
Fe	85000	2.7	341		0.40	2.8
Ni	1300	.06	150		11.5	17
Cu	1700	.06	170		10.0	14
Zn	5500	.10	180		3.3	5.4
Pb	2500	.09	170		6.8	10

CHAPTER VI

RESULTS

Table VI.1 gives the observed elemental loadings and total aerosol mass for the experiments conducted during this study. A statistical summary of these data is found in Table VI.2, which presents the basic statistics for both the absolute concentrations and the elemental loadings as a percentage of the total aerosol mass, hereafter referred to as the elemental percentages. Table VI.3 contains the interelement correlations for both the absolute concentrations and the elemental percentages. These last two tables are the basic data set used to determine the parameters of the factor model.

The initial step in the application of the model was a critical review of the data. This lead to the exclusion of four elements from the factor model. The principal factor solution was then found for the correlation matrix of the remaining elements. Next, an initial hypothesis was formed as to the sources of aerosol and their elemental composition. The algorithms of Chapter III were then used to rotate the principal factor solution so that its factors corresponded to the standardized sources. The final factor solution was transformed into a new source matrix. This source matrix is the set of parameters of the factor model. Finally, the correlation matrix predicted by the model was compared to the actual correlation matrix as a check on the mathematical computations.

Table VI.1

CONCENTRATIONS OF ELEMENTS IN PORTLAND AEROSOL SEPTEMBER 1975

(Microgm/m^3

Exper. No.	5	6	7	8	9	10	11	12	13	14	14A	14B	15	16	16A
Al	1.512	2.558	1.371	2.429	2.410	2.443	2.200	1.688	1.110	0.407	1.521	2.144	0.969	1.367	0.712
Si	4.325	6.808	4.307	6.907	6.517	6.885	5.328	4.339	2.683	1.929	3.655	6.441	3.347	3.631	2.863
Cl	0.242	0.078	0.014	0.094	0.024	0.378	0.067	0.019	0.900	1.109	0.388	0.803	0.281	0.850	0.110
K	0.785	1.176	0.770	1.160	1.088	1.225	0.973	0.841	0.446	0.300	0.741	0.848	0.599	0.492	0.570
Ca	2.302	3.027	2.352	3.656	2.671	2.874	2.091	2.120	1.556	0.942	1.931	2.260	1.624	2.048	1.575
Fe	5.570	6.057	3.895	7.494	6.047	5.257	3.672	4.087	2.761	1.719	3.772	4.444	3.666	4.125	2.917
Ti	0.351	0.589	0.371	0.555	0.484	0.469	0.437	0.440	0.248	0.296	0.312	0.415	0.298	0.324	0.319
V	0.029	0.061	0.028	0.051	0.059	0.069	0.063	0.027	0.019	0.014	0.035	0.082	0.060	0.038	0.020
Cr	0.141	0.149	0.039	0.289	0.256	0.251	0.051	0.106	0.067	0.052	0.148	0.260	0.083	0.045	0.064
Mn	0.290	0.337	0.168	0.376	0.359	0.241	0.160	0.192	0.145	0.088	0.226	0.206	0.183	0.135	0.148
Ni	0.070	0.102	0.028	0.093	0.090	0.110	0.052	0.048	0.035	0.015	0.077	0.114	0.037	0.046	0.060
Cu	0.072	0.072	0.069	0.101	0.081	0.085	0.086	0.081	0.061	0.028	0.069	0.064	0.066	0.127	0.097
Zn	0.357	0.302	0.189	0.370	0.379	0.263	0.108	0.168	0.199	0.113	0.281	0.233	0.206	0.306	0.174
Pb	1.233	1.744	1.615	1.625	1.615	2.464	1.777	1.167	1.178	1.035	1.406	1.278	0.960	1.945	1.484
Total Mass	103.7	141.9	127.5	159.3	156.9	154.8	125.8	122.8	83.5	47.8	99.6	143.5	111.9	87.0	110.8

* See Table IV.1 for dates and conditions.

Table VI.2

CONCENTRATIONS OF ELEMENTS IN PORTLAND URBAN AEROSOL SEPTEMBER, 1975

ELEMENT	MEAN		STD. DEVIVATION	
	$\mu g/m^3$	PERCENT	$\mu g/m^3$	PERCENT
Al	5.08	4.08	2.08	1.07
Si	14.4	11.78	5.01	1.86
Cl	0.318	0.377	0.355	0.621
K	0.826	0.674	0.277	0.101
Ca	2.25	1.87	0.674	0.301
Fe	4.48	3.72	1.48	0.794
Ti	0.404	0.347	0.096	0.088
V	0.045	0.037	0.021	0.012
Cr	0.138	0.109	0.091	0.053
Mn	0.222	0.183	0.088	0.049
Ni	0.067	0.054	0.031	0.018
Cu	0.078	0.067	0.022	0.025
Zn	0.246	0.210	0.091	0.077
Pb	1.52	1.33	0.397	0.428
TOTAL MASS	122		30.8	

Table VI.3

THE CORRELATION MATRIX OF THE CONCENTRATIONS

	Total	Pb	Zn	Cu	Ni	Mn	Cr	V	Ti	Fe	Ca	K	Cl	Si	Al
Al	0.850	0.570	0.508	0.297	0.794	0.747	0.714	0.743	0.882	0.810	0.870	0.944	-0.408	0.969	1.000
Si	0.904	0.546	0.520	0.244	0.837	0.764	0.792	0.779	0.891	0.832	0.892	0.941	-0.371	1.000	
Cl	-0.622	0.147	-0.174	-0.271	-0.164	-0.512	-0.102	-0.070	-0.477	-0.460	-0.495	-0.593	1.000		
K	0.906	0.564	0.469	0.236	0.767	0.794	0.707	0.647	0.895	0.818	0.890	1.000			
Ca	0.840	0.549	0.680	0.425	0.708	0.845	0.707	0.511	0.865	0.948	1.000				
Fe	0.769	0.381	0.831	0.393	0.708	0.938	0.749	0.482	0.793	1.000					
Ti	0.788	0.451	0.409	0.209	0.658	0.759	0.620	0.533	1.000						
V	0.696	0.371	0.253	0.114	0.696	0.415	0.612	1.000							
Cr	0.717	0.257	0.648	0.067	0.865	0.767	1.000								
Mn	0.718	0.218	0.821	0.177	0.711	1.000									
Ni	0.739	0.448	0.598	0.211	1.000										
Cu	0.329	0.563	0.385	1.000											
Zn	0.437	0.262	1.000												
Pb	0.463	1.000													
Total	1.000														

THE CORRELATION MATRIX OF THE PERCENTAGES

	Pb	Zn	Cu	Ni	Mn	Cr	V	Ti	Fe	Ca	K	Cl	Si	Al
Al	-0.057	0.155	-0.015	0.552	0.340	0.355	0.434	-0.086	0.434	0.476	0.761	-0.313	0.820	1.000
Si	0.147	0.230	-0.158	0.505	0.391	0.517	0.471	0.310	0.495	0.574	0.680	0.120	1.000	
Cl	0.726	0.328	0.206	-0.191	-0.048	0.015	0.044	0.810	0.083	0.219	-0.266	1.000		
K	-0.072	0.041	-0.333	0.436	0.536	0.389	0.096	0.138	0.371	0.426	1.000			
Ca	0.436	0.712	0.374	0.223	0.580	0.194	-0.117	0.399	0.871	1.000				
Fe	0.160	0.849	0.307	0.342	0.801	0.345	-0.035	0.214	1.000					
Ti	0.622	0.215	0.045	-0.233	0.179	-0.026	-0.156	1.000						
V	-0.066	-0.072	-0.092	0.305	-0.127	0.221	1.000							
Cr	-0.281	0.275	-0.431	0.704	0.568	1.000								
Mn	-0.153	0.670	-0.167	0.456	1.000									
Ni	-0.139	0.338	-0.066	1.000										
Cu	0.604	0.490	1.000											
Zn	0.384	1.000												
Pb	1.000													

A critical analysis of the data base follows. In the discussion in Chapter III it was shown that the correlation of two uncorrelated elements must be about 0.5. Examination of the correlation matrix of elemental loadings shows that most of the elements do correlate with each other at the 0.4 level or higher. The notable exceptions are chlorine, titanium, vanadium and copper. The behavior of vanadium is easily explained. The amounts of vanadium present in the samples are near or below the minimum detectable limit of the X-ray fluorescence analysis, 25 ng/m^3. This means that the vanadium numbers are noise, random numbers that do not correlate with anything.

The case of copper and titanium is somewhat different. A number of their correlations are less than 0.4. This could be due to statistical fluctuation. However, the final decision to exclude these elements from the model was based on the possibility of contamination of the samples. Titanium is found in the plastic slide mounts used to hold the samples for X-ray analysis and copper aerosol is said to be produced by waring of the brushes of the motors of the high volume air pump used during the experiment.

The behavior of the chlorine loadings presents a more interesting problem. The chlorine loadings are negatively correlated with most other elements and are extremely variable, their standard deviation is actually greater than their mean. The key to the explanation of this is found in the large negative correlation of chlorine and total mass loading. Chlorine is a tracer for clean marine air because the sea salt aerosol carried by marine air is rich in sodium chloride. With an influx of clean Pacific air, the levels of most elements and the total mass load would decrease, but the chlorine levels would increase. This would explain the observed negative correlations. In order to test this hypothesis, size resolved aerosol samples obtained from a Lundgren impactor were analyzed for days when the chlorine was high and the total mass low. Most of the chlorine was found to be associated with large particles, those greater than one micron in diameter. This is consistent with the known size distribution of sea spray (Bifford, 1970). This anomalous behavior of chlorine is the reason it was not considered in the factor analysis or the element balance. This problem could be alleviated by the subtraction of background aerosol elemental loadings.

Finally, it was decided to exclude lead from the factor analysis but not the final element balance. This was done because lead is the only element in this analysis that is predominately associated with the auto source. Other elements associated with auto exhaust are chlorine, zinc, and iron. Chlorine has already been removed from consideration and the absolute amounts of zinc and iron contributed by auto exhaust are a very small part of the total loadings of these elements. Consequently, lead should not correlate highly with any of the elements and its exclusion from the factor model should have little effect. A factor solution containing lead was produced and this was found to be the case.

The next step in obtaining the factor model is to find the principal factor solution. To do this the eigenvalues and eigenvectors of the correlation matrix of the nine remaining elements, as a percentage of the aerosol, were found. Some of the variation of the elemental percentages is due to error of analysis and sample collection. Recall from the discussion of factor analysis in Chapter II that the total variance of the normalized element i is

$$\alpha_{ij}^2 + \sigma_{\text{error}}^2 = 1 .$$

Where the α_{ij} are the factor loadings, and σ_{error}^2 is the fraction of the total variance of element i due to sampling and analysis errors. Thus, the fraction of the variance of an element explained by the factor model is $1 - \sigma_{\text{error}}^2$. The diagonal of the correlation matrix contains the correlation of an element with itself, or its variance. Thus, the diagonal contains $1 - \sigma_{\text{error}}^2$ rather than one. The σ_{error}^2 for each element are taken from the error analysis of Chapter V. The final correlation matrix used is given in Table VI.4(A). The nine eigenvalues and eigenvectors of this modified correlation matrix are seen in Table VI.5.

The corresponding factors are given in Table VI.6. Note that the first four factors explain 96% of the variance not due to experimental error. The model is restricted, without much loss of information, to these four principle factors.

The algorithms developed in Chapter III require that an initial source matrix be assumed. Except for the tracer elements, the composition of the source need not be accurately known. This is because the algorithms will produce a new source matrix that is consistent with the observed correlations. All that is required is an initial guess. The initial source matrix used in the calculations is given in Table VI.7.

Table VI.4

ORIGINAL MODIFIED CORRELATION MATRIX

(x 1000)

	Al	Si	K	Ca	Fe	Cr	Mn	Ni	Zn
Al	841								
Si	820	928							
K	761	680	800						
Ca	476	574	426	931					
Fe	434	495	371	871	961				
Cr	355	517	389	194	345	954			
Mn	340	391	536	580	801	568	938		
Ni	552	505	436	223	342	704	456	904	
Zn	155	230	041	712	849	275	670	338	967

(A)

REPRODUCED CORRELATION MATRIX

(x 1000)

	Al	Si	K	Ca	Fe	Cr	Mn	Ni	Zn
Al	822								
Si	849	886							
K	709	712	761						
Ca	498	577	358	768					
Fe	419	505	358	813	950				
Cr	411	440	464	260	379	793			
Mn	335	387	467	559	775	578	888		
Ni	494	536	416	323	364	726	420	769	
Zn	131	227	016	701	847	274	610	300	926

(B)

Table VI.5

EIGENVALUES AND EIGENVECTORS OF THE MODIFIED CORRELATION MATRIX

VALUES x 1000									
FACTOR	1	2	3	4	5	6	7	8	9
Al	327	-354	-315	-167	255	-223	-211	-499	-481
Si	355	-307	-260	-256	-442	-400	238	478	079
K	307	-341	-245	478	216	173	220	-186	584
Ca	353	296	-365	-135	-198	719	148	041	-238
Fe	386	370	-095	025	-022	-135	-757	103	319
Cr	290	-281	599	050	-576	151	-095	-371	008
Mn	368	198	226	635	133	-192	151	282	-463
Ni	300	-267	445	-395	532	264	-039	359	049
Zn	299	525	152	-312	148	-310	471	-361	213
EIGEN-VALUE	4.825	1.661	1.017	0.435	0.275	0.064	0.027	-0.002	-0.074

Table VI.6

PRINCIPAL FACTOR SOLUTION

VALUES x 1000							
FACTOR	1	2	3	4	5	6	7
Al	717	-457	-318	-110	134	-056	-032
Si	781	-396	-263	-169	-232	-101	035
K	675	-440	-247	315	113	044	033
Ca	776	381	-368	-089	-104	182	022
Fe	847	477	-095	016	-012	-034	-113
Cr	637	-297	604	033	-302	038	-014
Mn	808	255	227	419	070	-049	022
Ni	660	-344	449	-260	279	067	-006
Zn	656	676	153	-206	077	-078	070
EIGEN VALUE	4.825	1.661	1.017	0.435	0.275	0.064	0.022
% VARIANCE	58.1	20.0	12.3	5.2			
CUMULATIVE % VARIANCE	58.1	78.2	90.4	95.7			

Table VI.7

THE INITIAL SOURCE MATRIX

	WEIGHT PERCENT				
ELEMENT	STREET DUST	METAL-LURGICAL	AUTO-MOTIVE	FUEL OIL	PLATING
Al	5.4	2.5	—	0.1	—
Si	20.0	0.1	—	1.0	—
K	0.54	1.0	—	0.1	—
Ca	1.6	1.0	—	1.0	—
Fe	5.6	30.0	0.5	6.0	—
Cr	.005	1.0	—	0.1	20.0
Mn	.131	2.5	—	0.1	1.0
Ni	.005	0.5	—	2.0	5.0
Zn	.03	2.0	0.5	0.1	1.0
Pb	.28	1.0	40.0	0.1	—

The composition of the dust source is taken from Table V.4. The metallurgical source composition is taken from Winchester and Nifong (1971) and Lee et al. (1975). The automotive source is that used by Friedlander (1973), and the fuel oil source is a composite based upon all the above references. The reasons for including a plating source are discussed later. The composition given in Table VI.7 is based on the assumption that the plating aerosol is 40% chromic acid mist. This assumption is for purposes of calculation only since no data from the literature are available.

Using the techniques of Chapter III, the dust, metallurgical and plating standardized sources are expressed as linear combinations of the four principal factors. The coefficients of this expansion are given in Table VI.8. Next, the principal factors are rotated so that the new factors will be close to the source factors derived from the initial source matrix. The necessary rotations are given in Table VI.9.

The minimization technique developed in Chapter III, equation (22) is used to refine the solution. The standard deviation of the sources were estimated from single tracer elements. The sources and tracers are: iron, metallurgical; silicon, street dust; chromium, plating. The final factor solution is shown in Table VI.10. The fourth factor is highly correlated with zinc, therefore it is referred to as the zinc factor. This factor was not derived a priori but is simply the remaining factor necessary to explain the observed correlations of the elemental percentages.

The reasons for assigning the chromium source to plating are persuasive but inconclusive. As an air pollutant, chromium is usually

Table VI.8

CORRELATIONS OF PRINCIPAL FACTORS AND SOURCES

VALUES x 1000				
PRINCIPAL FACTOR	STREET DUST	METAL-LURGICAL	FUEL OIL	PLATING
1	547	671	113	200
2	-239	405	-130	-252
3	-723	574	303	727
4	062	643	-409	-267

Table VI.9

ROTATIONS OF THE PRINCIPAL AXIS SOLUTION TO ALINE SOURCES WITH FACTORS

Step No.	Rotate Factors	Angle (degrees)	Comments
1	1, 2	31.11	
2	1, 3	36.22	
3	1, 4	33.5	Factor 1 is now the Metallurgical Source Factor
4	3, 7	180	Invert Factor 3
5	3, 2	-31.75	
6	3, 4	8.23	Factor 3 is now the Street Dust Factor
7	2, 4	180	Invert Factors 2 and 4
8	2, 4	37.05	Factor 4 is now the Plating Factor

Table VI. 10

FINAL FACTOR SOLUTION

VALUES x 1000

ELEMENT	METAL-LURGICAL	STREET DUST	PLATING	ZINC
Al	-029	710	520	216
Si	001	714	526	316
K	232	685	479	-093
Ca	310	469	057	670
Fe	600	381	042	666
Cr	453	008	759	108
Mn	842	272	223	235
Ni	193	026	798	307
Zn	513	003	-061	812

derived from metallurgical sources and combustion of residual fuel oils. The combustion source is ruled out in this case because residual oils all contain much more vanadium than chromium (Magee, et al., 1973). There is simply not enough vanadium observed in the aerosol to explain more than a small fraction of the chromium. Furthermore, it is shown below that the metallurgical source can explain no more than half of the chromium observed. There are also positive reasons for suspecting plating operations as a source of chromium. Nickel is highly correlated with chromium in the aerosol and since nickel is also used in the plating industry this would be a possible basis for this correlation. Furthermore, there are about thirty companies in the Portland area engaged in plating operations, according to the Yellow Pages and the Oregon Directory of Manufacturers. Air pollution control equipment exists for this industry (Danielson, 1973), but it is not installed (Dave Harbert, Engineer, Oregon Department of Health, personal communication). A moderate sized plating tank has been observed to produce .45 pound of chromic acid mist per hour (Danielson, 1973, p. 330). It seems possible that this industry is contributing a large amount of the chromium in Portland aerosol; if not a large quantity of the total particulate loading.

The new source matrix is calculated using the above mentioned tracers and formula III(13). It is assumed for purposes of this calculation that the plating source is one percent chromium and that the zinc source is one percent zinc. The resulting source matrix is seen in Table VI.11. This source matrix differs from the initial source matrix in several particulars. The dust source is richer in aluminum,

Table VI.11

SOURCE MATRIX DERIVED FROM THE FACTOR MODEL

WEIGHT PERCENT				
ELEMENT	DUST	METAL-LURGICAL	PLATING	ZINC
Al	9.4	—	10.5	2.7
Si	20.0	0.1	22.5	8.4
K	0.79	1.0	0.84	—
Ca	2.1	5.4	0.40	2.9
Fe	5.0	30.0	0.84	8.3
Cr	0.007	1.5	1.0	0.09
Mn	0.21	2.4	0.26	0.17
Ni	0.007	0.19	0.32	0.07
Zn	0.004	2.5	—	1.0

calcium and manganese than in the initial source matrix. This may be due to fractionation effects of aerosol suspension. The metallurgical source is enriched in calcium and depleted in aluminum over the initial assumptions. The plating source contains a surprising amount of aluminum and silicon. The deduced source loadings are directly proportional to the assumption of the percentage of chromium in the source. If the plating source is really 10% chromium, then its aluminum loading would be over 100%. This is not feasible. One percent is used for the loading of chromium in the plating source and zinc in the zinc source because it is a value that gives reasonable numbers and can be easily scaled to some other value.

This source matrix, as deduced from the factor analysis, explains the correlations of the elements. Table VI.4(B) gives the correlation matrix reproduced from the factors in Table VI.10. The formula used is

$$r(i,j) = \sum_{k=1}^{w} \alpha_{ik}\alpha_{jk} ,$$

where

$r(i,j)$ = correlation of element i and element j,

and

α_{ik} = loading of element i on factor k.

Perfect agreement with the observed correlation matrix is not expected since only four factors are used; however, the degree of agreement is certainly within the range one would expect for statistical variation in a small sample. The similarity of the numbers of the two matrices is a check on the accuracy of the calculations, an important consideration when performing many complicated mathematical manipulations.

CHAPTER VII

CONCLUSIONS AND DISCUSSION

The basic purpose of this study was to construct a statistical model of an urban aerosol that would relate known sources to observed elemental concentrations and correlations. Consequently, the emphasis of this dissertation has been on the development of the model. In the course of this development a basic method was derived which links the factor solution to a physical model, the chemical element balance model. The physical model must have a firm theoretical basis; in this study the Gifford-Hana model is that basis. If no physical significance can be placed on the parameters of the factor solution then there can be no criterion for the rational rotation of the principle factor solution and no real information can be gained from the model. It must also be remembered that the factor model is just a multivariate linear model. Any attempt to model nonlinear situations is hopeless unless a change of variable, such as a logarithmic transformation, is made.

The strongest argument in favor of the factor model is also the simplest. The correlations of the elements in the aerosol are adequately explained by only four factors. This basic observation belies the underlying structure of the sources of the aerosol. Such simplicity evident in a system of great complexity strongly suggests the presence of a physical relationship. This is borne out by a closer examination of the results.

One could describe the factor model as a second order model, in the sense that it explains variances and correlations as well as average values. The advantages of this are seen if the predictions of the factor model are compared to the predictions of a simple element balance using the source matrices that have already been introduced. A standard element balance was done using the factor model source matrix, Table VI.11. The initial source matrix, Table VI.7 and the source matrix of Gatz, Table II.1. The calculations were based upon a linear programming solution to the element balance constraints as described in Chapter II. A list of the three solutions is given in Table VII.1. Although the factor model does not explicitly contain a fuel oil factor, the nickel not explained by the rest of the factors is assumed to be due to fuel oil combustion. The elemental make up of the fuel oil source is as given in the initial source matrix. Similarly, the automotive source is not included in the factor analysis; however, the auto source is included in the element balance by taking lead as a tracer for auto exhaust. The automotive source contribution is less for the factor and initial models than for Gatz's model because in the first two models some of the lead is assumed to come from street dust and metallurgical sources. The amount of lead in these two sources is taken to be the same for the factor model as the initial model, since there is no basis from which to calculate the lead loadings in the factor model.

Table VII.1

SOURCE CONTRIBUTIONS TO THE AEROSOL

	WEIGHT PERCENT		
	SOURCE MATRIX USED		
SOURCE	FACTOR MODEL	INITIAL MODEL	GATZ'S MODEL
STREET DUST	50	59	—
SOIL DUST	—	—	34
CEMENT DUST	—	—	2.8
AUTO EXHAUST	2.9	2.9	3.3
METALLURGICAL	4.0	4.0	6.7
FUEL OIL	0.5	2.8	0.9
PLATING	5	0.3	—
ZINC	11	—	—
TOTAL	73.4	69.0	47.7

The usual test of the effectiveness of an element balance is how well it explains the observed elemental loadings, particularly elements not used as tracers. Table VII.2 contains the predictions of all three element balances and the observed elemental loadings. The square root of the average squared percentage of error is used to compare the accuracy of each set of predictions. The factor model is the most effective in explaining the observed loadings, according to this measure.

Of course, the reason that the factor model does better is the inclusion of the hypothetical sources for chromium and zinc. The advantage in this is that the model gives some idea as to what kind of sources are needed to explain the zinc and chromium loadings. The simple element balance technique can only indicate that there is an error in the source matrix or that there is a missing source. The factor model predicts that the problem is a missing source; any error in the initial source matrix would have been corrected by the algorithms of Chapter III. This extra information deduced from the factor model is in the correlation matrix and, therefore, could not possibly come from a simple element balance.

Another example of the importance of the second order effects that are taken into account by the factor model is seen in comparing the fuel oil source loading predicted by the a priori initial model and that predicted by the factor model. The initial model assigns most of the nickel to fuel oil combustion. This is reasonable given the initial source matrix. However, if most of the nickel does indeed come from fuel oil combustion then there is no way to explain the high correlation

Table VII.2

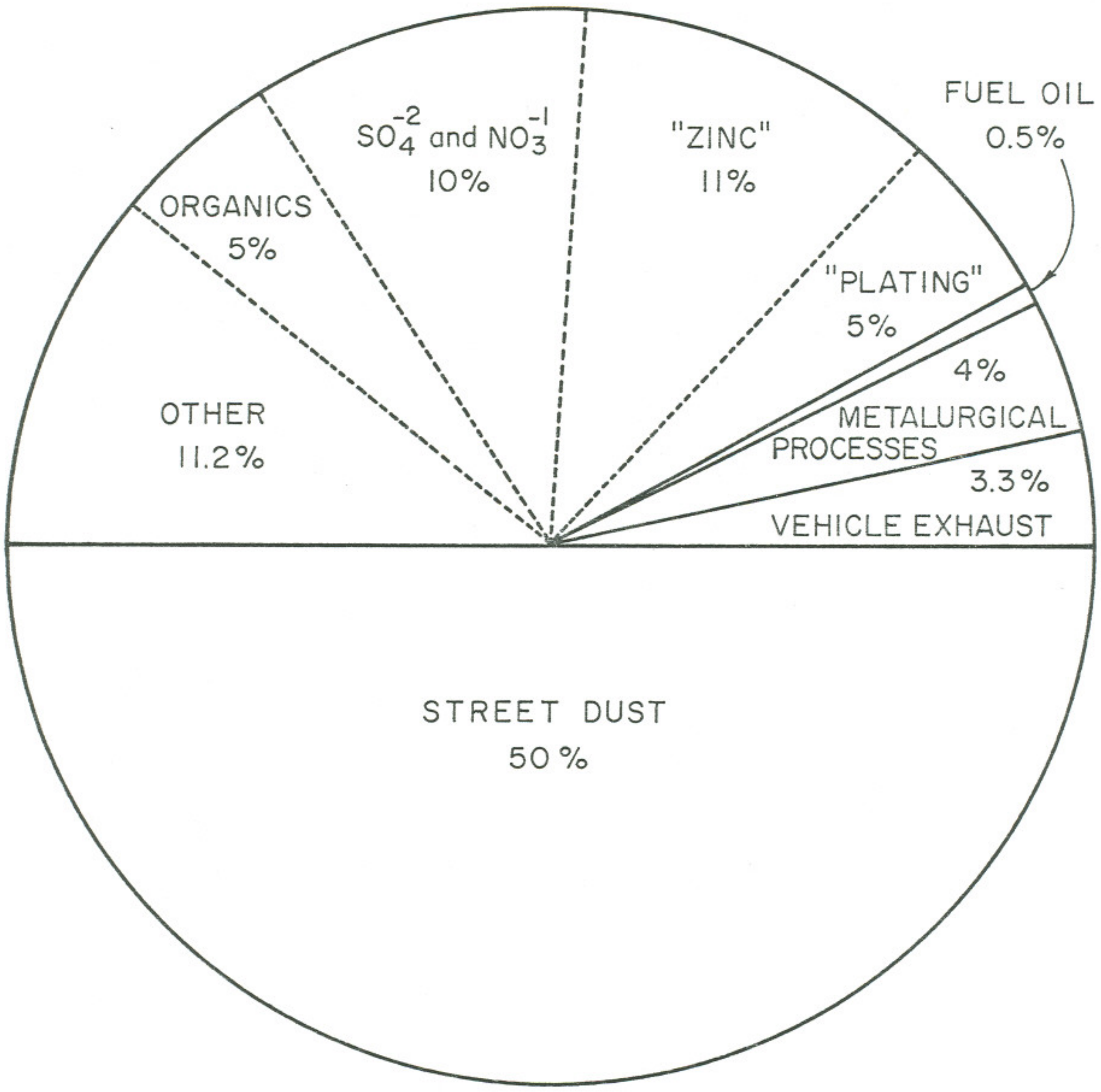
PREDICTED ELEMENTAL LOADING

WEIGHT PERCENT				
ELEMENT	FACTOR MODEL	INITIAL MODEL	GATZ'S MODEL	OBSERVED LOADING
Al	5.5	3.3	2.0	4.1
Si	12.1	11.8	—	11.8
K	.48	.36	.68	.67
Ca	1.6	1.0	1.9	1.9
Fe	4.7	4.7	3.7	3.7
Cr	.12	.11	.003	.11
Mn	.23	.18	.17	.18
Ni	.054	.074	.054	.054
Zn	.21	.12	.13	.21
Pb	1.33	1.33	1.33	1.33
ERROR	19.5	29.5	38.8	—

of chromium and nickel that is observed. One would have to make the unlikely assumption that the estimate of chromium in the fuel oil source is low by at least an order of magnitude in order to explain the chromium loadings as a result of the fuel oil emissions. The essence of this reasoning is that fuel oil cannot actually account for almost 3% of the aerosol. The factor model draws this conclusion automatically.

The final mass breakdown for the Portland aerosol September, 1975 is diagramed in Figure VII.1. The given amounts of sulfates, nitrates and organics are reasonable guesses based upon National Air Sampling Network data for Portland. The actual amount of the aerosol due to the hypothetical sources is not known. However, the factor model predicts that they represent real sources or assemblages of real sources. For this reason these sources are shown as part of the unaccounted fraction of the aerosol. The proportion of the aerosol due to vehicles includes diesel as well as auto exhaust. The scaling factor of 1.13 is derived from Table I.1.

The fraction of the aerosol explained by the hypothetical sources is inversely proportional to the percentage of the tracer element assumed to be in the source. Since nothing is known of the actual amount of zinc or chromium in the hypothetical sources, the assumption of a value of one percent was made arbitrarily. The amount of the element explained by the source is independent of this assumption because if the percentage of the tracer in the source increases, then the source loading decreases proportionately. It is quite possible, or even likely, that the fraction of the aerosol explained by the hypothetical sources is closer to 6% than 16% as shown in Figure VII.1. In



PORTLAND URBAN AEROSOL
SEPTEMBER, 1975

COMPONENTS SHOWN WITH DOTTED LINES
WERE NOT DIRECTLY OBSERVED.

Figure VII.1

lieu of more information the above caveat must suffice. Even if only a small part of the total aerosol is shown to be due to the hypothetical sources, their predicted existence and composition is one of the major strengths of the factor model.

Another test of the factor model is the comparison of its results with those arrived at by the emission inventory approach. Table I.1 contains a summary of a recent emission inventory for the Portland area. This source inventory does not include entrained dusts or secondary aerosols which account for 60% of the aerosol mass in the factor model. Thus, division of the emission inventory results by a correction factor of $1/(1 - .6) = 2.5$ is necessary in order to compare the two results meaningfully. Industrial processes account for 76% of the particulate included in the emission inventory and $76/2.5 = 30\%$ of the aerosol. The sum of the zinc, plating and metallurgical sources is 20%. The agreement is acceptable considering that the emission inventory was calculated on a yearly basis and the factor model is derived from data for one month only. This explains the lack of agreement between the residual fuel oil emissions given by the two methods. Over a year the industrial fuel oil emissions account for about 2% of the particulate. As measured in September by the factor model this number is only 0.5% Such a low value is reasonable because many industries use natural gas when it is available in the summer instead of fuel oil. On the other hand, the vehicular source strength should be fairly constant throughout the year. The agreement between the emission inventory and the factor model in this case is rather good, the source strength being 3.2% and 4.8% in the factor model and the inventory respectively. There is no serious disagreement between the two approaches. However, the fact that 60% of the aerosol is not included in the emission inventory is a powerful argument in favor of source identification by direct measurements of the aerosol.

The factor model does have its weaknesses; however, included in the discussion of these are suggestions for further research in this area. The major structural defect is the assumption of statistical independence of the factors. For the data set collected in this study this assumption is justifiable. The use of one day averages smooths out the effects of the diurnal pattern of urban pollution. A large amount of the variation of the sources seen at the sampling site is due to variations in the wind direction giving rise to a varying mix of sources in the aerosol. This helps randomize the sample and eliminate any false correlations. However, it is conceivable that two sources could be truly correlated. The model can be extended to cover this case by the use of oblique rather than orthogonal factors. There is no great difficulty in this; the algorithms developed to rotate the principle factor solution could be quite easily modified to cover this possibility. The only a priori information necessary would be a knowledge of which sources are correlated.

The other major omission of the factor model, as presently formulated, is the exclusion of secondary aerosols from consideration. There is no reason why one or more hypothetical sources could not be included to explain the sulfate, nitrate and organic fractions of the aerosol. Collection and analysis of the background aerosol would also have been useful. Subtraction of the background aerosol elemental and mass loadings would remove problems such as encountered with chlorine in this study. In general, the low levels of background aerosol present in the Portland area do not significantly affect the urban aerosol. In a more heavily polluted area of the country subtraction of the background aerosol would be necessary for the successful application of a factor model. The background aerosol loading could be determined by sampling outside of the urban area.

The extension of the factor model to types of sources other than urban area sources would be of great interest. In particular, the problem of modeling a number of closely placed point sources is one which has not been dealt with successfully by the more traditional approaches. Indeed, some theoreticians believe that a dispersion model based on first principles will never be able to accurately describe real world situations (Scorer, 1968). The semiempirical nature of the factor analysis approach would be an advantage if this is true.

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APPENDIX A

The purpose of this appendix is to present a simple example of the use of factor analysis to uncover the underlying structure of a data set. To this end, an artificial data set consisting of fifteen observations of four variables was constructed. This data, given in Table A.1, was produced from the fifteen pairs of numbers in Table A.2. These values were drawn at random from a table of random numbers having a standard normal distribution, i.e., mean 0 and standard deviation 1. The psuedo-observations of the C_i were calculated from the equations,

$$\begin{aligned} & C_{1_j} = .300S_{1_j} + .050S_{2_j}, \\ & C_{2_j} = .200S_{1_j} + .200S_{2_j}, \\ & C_{3_j} = .050S_{1_j} + .075S_{2_j}, \\ \text{and} \quad & C_{4_j} = .025S_{1_j} + .400S_{2_j}, \\ \text{for} \quad & j = 1 \text{ to } 15. \end{aligned} \tag{1}$$

C_{ij} is the j^{th} observation of C_i, and S_{1_j}, S_{2_j} is the j^{th} pair of values of S_1 and S_2.

Thus, the C_i are generated by two factors. It is the task of this example to recover equations (1) from the correlation matrix of the simulated observed variables. This correlation matrix is obtained by the usual formula,

$$r(C_i, C_j) = \frac{\sum_{K=1}^{m} (C_{ik}-m_i)\ (C_{jk}-m_j)}{(m-1)\ S_i\ S_j}$$

Table A.1

SIMULATED DATA

	C_1	C_2	C_3	C_4
	0.195	0.118	0.031	-0.013
	0.315	0.521	0.084	0.764
	0.362	-0.218	0.014	-1.061
	-0.178	-0.085	-0.026	0.066
	-0.283	-0.202	-0.049	-0.055
	0.379	0.517	0.090	0.660
	0.179	0.200	0.038	0.205
	0.038	-0.216	-0.018	-0.572
	0.189	-0.079	0.011	-0.470
	-0.153	-0.238	-0.039	-0.335
	0.192	-0.045	0.015	-0.396
	0.108	0.218	0.033	0.356
	-0.249	-0.049	-0.030	0.256
	0.251	0.220	0.047	0.146
	-0.109	0.070	-0.004	0.330
mean	0.0824	0.0488	0.0131	- .0078
σ	0.2236	0.2489	0.0418	0.4879

Table A.2

NUMBERS USED TO SIMULATE THE DATA

0.738	1.865
0.661	- .073
1.665	-2.756
-0.629	0.204
-0.931	-0.079
0.999	1.587
0.518	0.481
0.370	-1.452
0.834	-1.227
-0.376	-0.813
0.215	-0.876
0.815	-1.048
-0.947	0.700
0.784	0.317
-0.505	0.856

where $r\ (C_i,\ C_j)$ = Correlation of C_i and C_j,

n = number of observations,

$$m_i = \frac{1}{n}\sum_{k=1}^{n} C_{ik}$$

and $$S_i = \left(\frac{1}{n-1}\sum_{k=1}^{m} (C_{ik}-m_i)^2\right)^{1/2}.$$

Table A.3 gives the correlation matrix for the simulated observables.

The next step is to produce a factor solution that explains the observed correlation matrix. The principal factor solution is found by diagonalizing the correlation matrix. The eigenvalues of this matrix are found to be:

2.894
1.106
.0003
.0003.

Clearly, the two factors corresponding to the first two eigenvalues are the only factors of any importance. The loadings of the C_i on each factor are calculated by dividing the eigenvectors by the square root of their eigenvalues. The eigenvectors and factor loadings are shown in Table A.4.

In this case the factor space is two-dimensional; therefore, it is possible to plot the principal factor representation of the C_i, Figure A.1 is this graph. In order to recover (1) the factors must be rotated. Some a prior information is required to pick the proper rotation. Suppose it is known that C_4 is virtually an

Table A.3

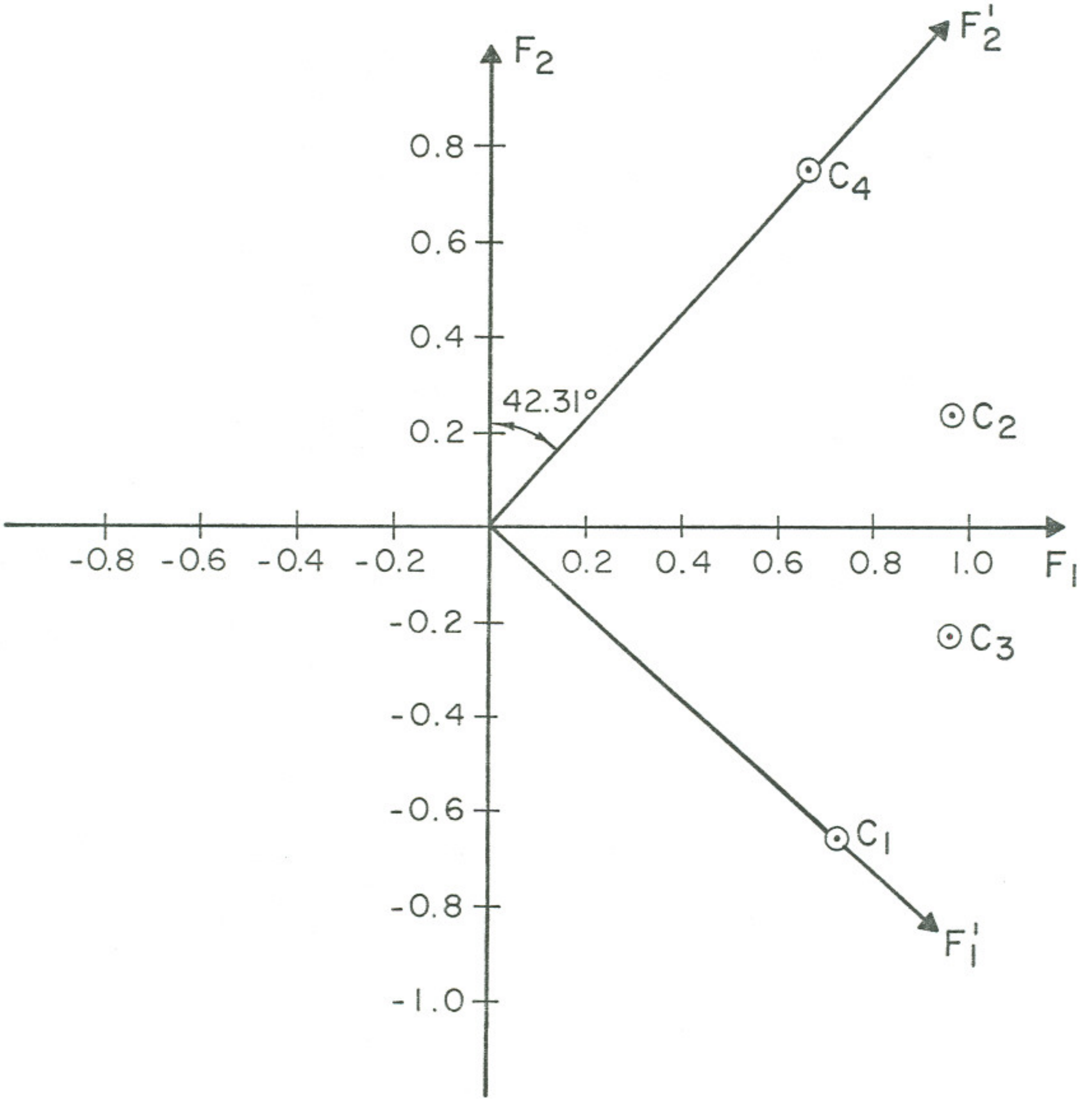
CORRELATIONS OF THE SIMULATED DATA

	C_1	C_2	C_3	C_4
C_1	1.00	.565	.871	-.003
C_2	.565	1.00	.897	.823
C_3	.871	.897	1.00	.488
C_4	-.003	.823	.488	1.00

Table A.4

PRINCIPAL FACTOR SOLUTION

Variable	Eigenvectors		Factor Loadings	
C_1	.434	-.642	.738	-.675
C_2	.573	.216	.974	.227
C_3	.573	-.215	.974	-.227
C_4	.396	.703	.673	.740



PRINCIPAL FACTOR REPRESENTATION

Figure A.1

independent variable, i.e., that one of its factor loadings is almost zero. The principal factors can then be rotated clockwise by 42.31 degrees, so that the new F_2 axis coincides with the factor representation of C_4. This is shown in Figure A.1. The rotated factor model is:

$$\begin{aligned} \tilde{C}_1 &= 1.00F_1 - .003F_2^1, \\ \tilde{C}_2 &= .568F_1^1 + .823F_2^1, \\ \tilde{C}_3 &= .873F_1^1 + .488F_2^1, \\ \text{and} \quad \tilde{C}_4 &= .000F_1^1 + 1.00F_2^1, \end{aligned} \qquad (2)$$

The $\tilde{C}_i$ represents the standard form of C_i. The relationship of $\tilde{C}_i$ and C_i is

$$\tilde{C}_i = \frac{C_i - \mu_i}{\sigma_i} \quad ,$$

where μ_i and σ_i are the mean and standard deviation of C_i. Thus,

$$C_i = \sigma_i \tilde{C}_i + \mu_i,$$

Therefore, to convert (2) to non standard form so it may be compared to (1), it is necessary to multiply each equation by σ_i and to add μ_i. Using the estimates to μ_i and σ_i derived from Table A.1,

$$\begin{aligned} C_1 &= .224F_1^1 - .00067\, F_2^1 + .0824, \\ C_2 &= .141F_1^1 + .205\, F_2^1 + .0488, \\ C_3 &= .036F_1^1 + .020\, F_2^1 + .0131, \\ \text{and} \quad C_4 &= .000F_1^1 + .488\, F_2^1 - .0078. \end{aligned} \qquad (3)$$

Comparing the coefficients of F_1^1 and F_2^1 with those of S_1 and S_2 in (1), it is seen that the agreement is fairly good. The error is due to the small sample size which was used to estimate the correlation matrix, means, and standard deviations. Also, note that some a priori knowledge of the desired solution was necessary to find the proper rotation of the principal factor solution.

APPENDIX B

Derivation of the correlation equation of Chapter III.

Using the notation of equation (9) and the following, the mean and standard deviation of the product of two independent variables are

$$\mu_{C_1} = E(C_1) = E(Y_1 M) = \mu_{Y_1}\,\mu_m ,$$

$$\begin{aligned}
\text{and}\quad \sigma_{C_1}^2 &= E(C_1^2) - \left[E(C_1)\right]^2 \\
&= E(Y_1^2 M^2) - \mu_{Y_1}^2\,\mu_m^2 \\
&= E(Y_1^2)\,E(M^2) - \mu_{Y_1}^2\,\mu_m^2 \\
&= (E(Y_1^2) - \mu_{Y_1})\,(E(M^2) - \mu_m^2) \\
&\quad + \mu_{Y_1}\,(E(M^2) - \mu_m^2) + \mu_m^2\,(E(Y_1^2) - \mu_{Y_1}^2) \\
&= \sigma_{Y_1}^2\,\sigma_M^2\left(1 + \left(\frac{\mu_{Y_1}}{\sigma_{Y_1}}\right)^2 + \left(\frac{\mu_m}{\sigma_m}\right)^2\right). \qquad (1)
\end{aligned}$$

The correlation of C_1 and C_2 is

$$\begin{aligned}
\gamma_{c_1, c_2} &= \frac{E\left[(C_1-\mu_{c_1})(C_2 - \mu_{c_2})\right]}{\sigma_{c_1}\,\sigma_{c_2}} \\
&= \frac{E(C_1C_2) - \mu_{c_1}E(C_2) - \mu_{c_2}E(C_1) + \mu_{c_1}\mu_{c_2}}{\sigma_{c_1}\,\sigma_{c_2}} .
\end{aligned}$$

Substitute for σ_{c_1} and σ_{c_2} from equation (1) to get

$$\frac{E(C_1C_2)-\mu_{c_1}\mu_{c_2}}{\sigma_{Y_1}\sigma_{Y_2}\sigma_m^2\left[\left(1+\left(\frac{\mu_{Y_1}}{\sigma_{Y_1}}\right)^2+\left(\frac{\mu_m}{\sigma_m}\right)^2\right)\left(1+\left(\frac{\mu_{Y_2}}{\sigma Y_2}\right)^2+\left(\frac{\mu_m}{\sigma_m}\right)^2\right)\right]^{1/2}} . \qquad (2)$$

But,

$$\begin{aligned} E\ (C_1\ C_2) &= E\ (Y_1 Y_2 M^2) \\ &= E\ (Y_1)\ E\ (Y_2)\ E\ (M^2) \\ &= \mu_{y_1}\ \mu_{y_2}\ (\sigma_m^2 + \mu_m^2)\ . \end{aligned}$$

Thus,

$$\begin{aligned} E\ (C_1 C_2) - \mu_{c_1}\mu_{c_2} &= \mu_{y_1}\mu_{y_2}\sigma_m^2 + \mu_{y_1}\mu_{y_2}\mu_m^2 \\ &\quad - \mu_{y_1}\ \mu_{y_2}\mu_m^2 \\ &= \mu_{y_1}\mu_{y_2}\sigma_m^2\ . \end{aligned}$$

Finally, equation (2) becomes

$$r_{c_1, c_2} = \frac{\mu_{Y_1}\mu_{Y_2}\sigma_m^2}{\sigma_{Y_1}\sigma_{Y_2}\sigma_m^2 \left[\left(1 + \left(\frac{\mu_{Y_1}}{\sigma_{Y_1}}\right)^2 + \left(\frac{\mu_m}{\sigma_m}\right)^2\right)\left(1 + \left(\frac{\mu_{Y_2}}{\sigma_{Y_2}}\right)^2 + \left(\frac{\mu_m}{\sigma_m}\right)^2\right)\right]^{1/2}}\ .$$

If

$$e_x = \mu_x / 1\sigma_x\ ,$$

then

$$r_{c_1, c_2} = \frac{e_{Y_1} e_{Y_2}}{[(1 + e_{Y_1}{}^2 + e_m{}^2)(1 + e_{Y_2}{}^2 + e_m{}^2)]^{1/2}}\ ,$$

which is the result required.

APPENDIX C

Derivation of equation (19) of Chapter III

Using the notation of equation (17) and the following,

$$V(\Theta) = N \sum_{i=1}^{N} (\alpha''_{i1} \cos \Theta + \alpha''_{iq} \sin \Theta)^2 - [\sum_{i=1}^{N} (\alpha''_{i1} \cos \Theta + \alpha''_{iq} \sin \Theta)]^2 ,$$

where

$$\alpha''_{ij} = \alpha_{ij}/_{hi} \; .$$

The derivative of V is

$$\begin{aligned} \frac{dV}{d\Theta} = N \sum_{i} 2(\alpha''_{i1} \cos \Theta + \alpha''_{iq} \sin \Theta)(-\alpha''_{i1} \sin \Theta + \alpha''_{iq} \cos \Theta) \\ -2[\sum_{i} \alpha''_{i1} \cos \Theta + \alpha''_{iq} \sin \Theta][\sum_{i} (-\alpha''_{i1} \sin \Theta + \alpha''_{iq} \cos \Theta)] \end{aligned}$$

$$\begin{aligned} = N \sum [(\alpha''^{2}_{iq} - \alpha''^{2}_{i1}) 2 \cos \Theta \sin \Theta + 2\, \alpha''_{i1}\alpha''_{iq} (\cos^2 \Theta - \sin^2 \Theta)] \\ - \sum_{i} \sum_{j} [(\alpha''_{iq}\alpha''_{jq} - \alpha''_{i1}\alpha''_{j1})\, 2 \cos \Theta \sin \Theta \\ + 2(\alpha''_{i1}\alpha''_{jq} + \alpha''_{j1}\alpha''_{iq})(\cos^2 \Theta - \sin^2 \Theta)] \; . \qquad (1) \end{aligned}$$

Using the identities

$$\sin 2\Theta = 2 \cos \Theta \sin \Theta ,$$

and

$$\cos 2\Theta = \cos^2 \Theta - \sin^2 \Theta .$$

(1) becomes

$$\begin{aligned}\frac{dv}{d\Theta} = N[(\sum_i (\alpha_{iq}''^2 - \alpha_{i1}''^2))\sin 2\Theta + 2(\sum_i \alpha_{i1}'' \alpha_{iq}'') \cos 2\Theta] \\ -[\sum_i \sum_j (\alpha_{iq}'' \alpha_{jq}'' - \alpha_{i1}'' \alpha_{j1}'')] \sin 2\Theta \\ + 2[\sum_i \sum_j (\alpha_{i1}'' \alpha_{jq}'' + \alpha_{j1}'' \alpha_{iq}'')] \cos 2\Theta . \qquad (2)\end{aligned}$$

The first double sum in the above equation is

$$\sum_i \sum_j (\alpha_{iq}''\alpha_{jq}'' - \alpha_{i1}''\alpha_{j1}'') = (\sum_i \alpha_{iq})^2 - (\sum_i \alpha_{i1})^2 ,$$

and the second double sum is

$$\sum_i \sum_j (\alpha_{i1}''\alpha_{jq}'' + \alpha_{j1}''\alpha_{iq}'') = 2(\sum_i \alpha_{i1}'')(\sum_i \alpha_{iq}'') .$$

Thus, setting the derivative to zero and collecting Terms in sin 2Θ and cos 2Θ equation (19) of Chapter III is obtained.

VITA

Ronald Claude Henry was born in Dawson Creek, British Columbia, Canada, on September 7, 1945. He was awarded a B.S. degree in science in 1966 from Stevens Institute of Technology, Hoboken, New Jersey. In 1968 an M.A. degree in mathematics was conferred on him by the University of Southern California, Los Angeles, California. Following graduation from the University of Southern California, he became a member of the technical staff of Bell Telephone Laboratories, Inc., Whippany, New Jersey, where he was involved in classified work on the SAFEGUARD anti-ballistic missile system. He left this position in 1970 to become a Peace Corps volunteer to Malaysia in which capacity he taught mathematics, chemistry, general science, and technical drawing at Sabak College on the island of Borneo. He began graduate studies in applied physics in the Winter of 1973 at the Oregon Graduate Center. In 1974 he was awarded the Gottesman Fellowship. He is a member of the Sigma Xi honor society. His scientific interests lie in the domain of environmental science and technology with special emphasis on the analysis and interpretations of air pollution data.