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A coaxial-conical, converging-channel, ion mobility spectrum analyzer has been constructed and a series of measurement were made in an urban environment. In order to determine if air ion mobilities could be used to determine concentration of air pollutions, a regression analysis was performed on the mobility measurements and specific air pollutiant concentrations; some degree of correlations were found but results are inconclusive at this point.

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The Use of Air Ion Mobility Spectrum Analysis to Determine Air Pollution

by

Jon Alan Arnold

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

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The Use of Air Ion Mobility Spectrum Analysis to Determine Air Pollution by Jon Alan Arnold

The objective of the investigation was to determine if air ion concentrations could be used to determine the concentrations of air pollutants. A coaxial-conical, converging channel ion mobility chamber was constructed and a series of extensive measurements were made. A regression analysis was used to determine if the ion concentrations were correlated to the air pollutant concentrations. Some degree of correlation was found for two air pollutants. The potential use of air ion measurements to determine air quality still remains to be proven.

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Introduction

In recent years the extent and effects of air pollution have become topics of major interest. One of the greatest problems associated with air pollution is that of monitoring the quality of the air. It is the purpose of this thesis to investigate the potential of using an air ion monitor to measure air quality.

The Nature of Air Ions

Air ions are a natural constituent of the atmosphere. These ions are responsible for the conductivity of the atmosphere and possibly for a variety of other phenomena that are not as well understood. Some investigations have been done on the interactions of air ions with atmospheric pollutants and artificial processes which affect air quality. These latter works give reason to believe that air ion concentration can be correlated to the concentration of atmospheric contaminants.

Air ions exist as electrically charged particles of dust, groups of molecules, or as single molecules. Ions consisting of a charged molecule are considered to be small, or highly mobile, ions. An ion's mobility refers to the net velocity an ion will attain in a unit electrical field. It has been assumed that air ions are singly charged; hence, an ion's mobility depends only upon its mass, shape, density, and its surrounding medium. Rich (1959) has lent theoretical verification to the assumption of unit charge for air ions on the basis of stability with relation to surface area and charge of the ion. A more massive ion with only its single charge will move more slowly than a less massive ion in the same electrical field. Ions have been classed as small, intermediate, and large, or Langevin, ions. Since ions are distributed over the size or mass spectrum continuously, the three classification are arbitrary and serve only to expedite discussion. The predominant charge carriers of the atmosphere are the small ions consisting of singly charged molecules or low mass molecular aggregates. The Langevin ions are probably condensation nuclei with masses thousands of times greater than the small ions. These two groups account for the great majority of air ions. In 1915, Pollack (1915) recognized the existence of intermediate ions. These ions are suspected of being transitional elements in that they grow to large ions.

Measurements of atmospheric conductivity by early workers eventually led to a more extensive knowledge of the "ion spectrum of the atmosphere". This term refers to the concentration of ions found at various mobilitites. The natural atmosphere has two principal "spectral lines"; the small ions and the large ions with the mobilities mentioned above. Between these two groups lies a region rather "sparsely and variably occupied by intermediate ions" and beyond the large ions lies a continuum of "ultra-large ions" (Israel, 1971). Israel (1971) has classified the ions into five groups according to their spectral regions, as shown in Table I.

Small ions

Small ions are usually formed by ionizing radiations, either high

	Designation	Mobility limits, cm^2/V sec	Size limits	Concentration extrema	Mean mobility, cm^2/V sec	Mean concentration
Priamry atmo-spheric ions	Small ions	$k \geq 1.0$	$r < 6.6 \times 10^{-8}$ cm	$n^{\pm}$ $100/cm^3$ to $n^{\pm}$ $2000/cm^3$	$k^{+} = 1.4$ $k^{-} = 1.75$	$n^{+} = 480/cm^3$ $n^{-} = 425/cm^3$
Second-ary atmo-spheric ions	Small intermediate ions	$1.0 > k \geq 0.01$	$6.6 < r < 78$			
	Large intermediate ions	$0.01 > k \geq 0.001$	$78 < r < 250$			
	Langevin ions	$0.001 > k \geq 0.00025$	$250 < r < 570$			
	Ultra-large	$k < 0.00025$	$r > 570$ (up to $r = 10^{-5}$cm)			

TABLE I: MOBILITY AND SIZE LIMITS OF INDIVIDUAL ION TYPES IN THE ATMOSPHERE energy photons or radioactive particles, which strike neutral gas molecules. These ions also originate from radioactive gases in the soil and from local disturbances such as lightning, X-rays, combustion processes, spashing water, and frictional electricity produced by drifting sand, dust, or snow. The concentrations of small ions are not equal near the surface of the Earth. The small positive ion concentration generally exceeds the small negative ion concentration due to a space charge formed by the Earth's electric field. The concentrations of the small ions undergo diurnal and seasonal variations and are also affected by meteorological conditions; see Table II. The mobilities of the small ions are affected by temperature and humidity. Humidity slows the negative ions while the positive ions show no dependence. Erikson (1927) suggested that this is due to differing affinities of negative and positive ions for water molecules.

Destruction of small ions occurs through loss of charge by combining with ions of opposite sign (recombination) or by losing its charge to the Earth or any surface. Average lifetimes of small ions vary from a few seconds in dirty air to five minutes in very pure air (Israel, 1971).

Intermediate and Large Ions

Intermediate and large ions are thought to be produced by the attachment of small ions to the particles of the atmospheric aerosol. Small ions do not gradually "grow" to form the larger ions since the molecular-sized small (primary) ion immediately forms the intermediate or large (secondary) ion upon attachment to an aerosol particle. This attachment process is shown schematically in Figure I. A definite

Meteorological parameter	Behavior of conductivity
Wind, strength	parallel variation
direction	differs locally, according to location of station
State of aerosol	
General visibility	parallel variation
Haze	lowered conductivity
Foehn	increased conductivity
Dust content	parallel variation
Fog	lowered conductivity
Cloudiness	
High clouds	no appreciable influence
Low clouds	increased conductivity
Rain	
Ordinary rain	negative conductivity usually higher positive conductivity unchanged
Thunderstorm rain	strong fluctuations; frequent increases in the negative and positive conductivity
Temperature, moisture, etc.	unclear, widely varying dependences from point to point
General meteorological situation	conductivity seems to be generally lower in high pressure areas than in low pressure areas

TABLE II: BEHAVIOR OF THE CONDUCTIVITY NEAR THE GROUND UNDER METEOROLOGICAL AND OTHER INFLUENCES

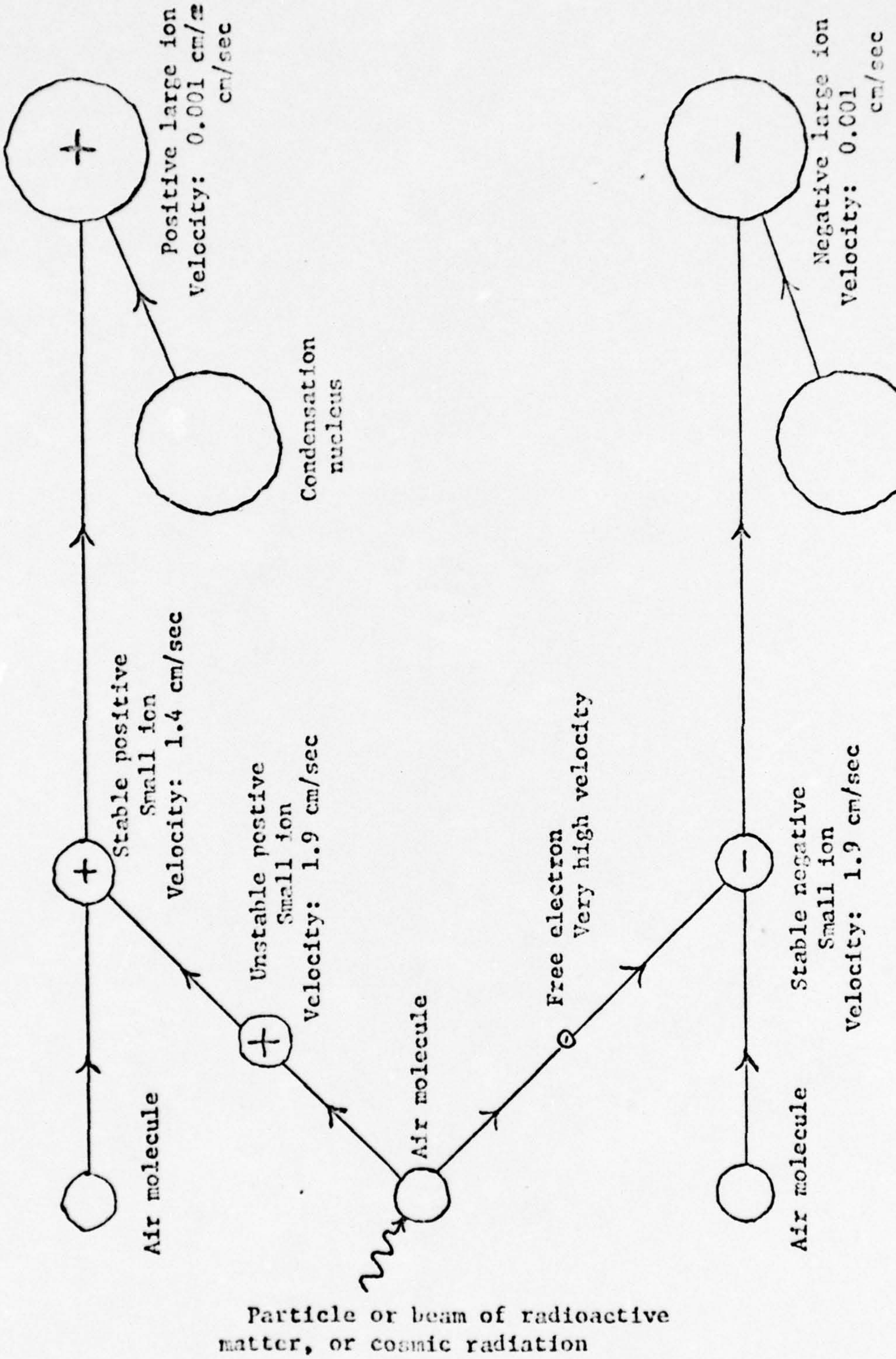

FIGURE I: SCHEMATIC REPRESENTATION OF ION FORMATION IN THE ATMOSPHERE minimum concentration of ions of mobilities in the ranges between the small and intermediate ions confirms the theory. Since the larger ions are formed from the atmospheric aerosol, it seems reasonable to use the existing studies of the aerosol to give information about large ions. The only difference will be in the ion's electrical charge.

Generally, studies of the aerosol have found large differences in the concentrations of suspension particles (also known as cloud condensation nuclei due to their role in cloud formation) depending on the locality. For representative numbers, see Table III. The aerosol concentration undergoes seasonal and diurnal variations. Meteorological variations are given in Table IV. The number densities of large ions are not much greater than the densities of small ions; hence, one can see that since the mobilities of the large ions are orders of magnitude less than the small ions, the conductivity of the atmosphere is due to the small ion content. However, as the lifetimes of the small ions are largely determined by the densities of the large ions and neutral aerosol particles, the conductivity follows inversely the large aerosol concentrations.

Intermediate and large ions are lost through recombinations or through meteorological cleansing actions such as precipitation, gravitational settling, and inertial separation.

Theoretical Considerations of Atmospheric Ion Interactions

The ionic state of the atmosphere is approached theoretically by grouping the ions into the three usual groups, assuming an equilibrium state exists and then writing simple equation that account for ion formation and recombination. Numerous authors have made attempts to

Measuring point	Mean	Mean maximum	Mean miniumum	Absolute maximum	Absolute minimum
Center of large city	147,000	379,000	49,100	4,000,000	3,500
Edge of large city	34,300	114,000	5,900	400,000	620
Land, interior	9,500	66,500	1,050	336,000	180
Land, coast	9,500	33,400	1,560	150,000	0
Mountains, 500-1,000 m	6,000	36,000	1,390	155,000	30
Mountains, 1,000-2,000 m	2,130	9,830	450	37,000	0
Mountains, above 2,000 m	950	5,300	160	27,000	6
Islands	9,200	43,600	460	109,000	80
Ocean	940	4,680	840	39,800	2

TABLE III: SURVEY OF THE ABUNDANCE OF CONDENSATION NUCLEI AT VARIOUS MEASURING POINTS, IN CM^{-3}

Reference element	Behavior of condensation nuclei (Z) and secondary ions (N)
Wind, strength	Variations in the same sense for low winds and in the opposite sense for strong winds
direction	Establishes the direct relationship with smoke and dust production from populated areas
Aerosol state, visibility	Variation in the opposite sense
Haze	High nuclei and secondary ion concentration
Foehn	Low concentrations of both
Dust content	Variation in the same sense
Fog air	Nonuniform, usually a reduction in Z and N
Precipitation, normal rain	Z and N usually decrease
Thunderstorm rain	N increases
Air masses	Dependence in densely populated areas and cities is weak, clearly recognizable in sparsely populated areas; behaviors in city and rural air are sometimes mutually opposite.

TABLE IV: THE DEPENDENCE OF SECONDARY IONS AND SUSPENSION CONCENTRATION IN THE ATMOSPHERE ON METEORLOGICAL FACTORS mathematically analyze fluctuations in ion concentrations. A partial list includes: Chalmers (1957), Neuberger (1951), Gunn (1955), Stergis (1954), Nolan and Doherty (1950), Keefe and Nolan (1962), and Keefe, Nolan, and Rich (1959).

The theoretical approach is not well justified as the assumptions made over-simplify the situation. The assumptions create a simple atmosphere that allows easy mathematical description, but when dealing with air pollution, complex atmospheres are met where such assumptions do not hold. The assumption of equilibrium is especially poor as it is known that the aerosol and large and small ion concentrations vary more rapidly than the time required to come to equilibrium. Equilibration times for large ions are estimated at thirty minutes (Israel, 1971) and small ions require a few minutes in even mildly polluted areas (Stergis, 1954). Steigerwald (1962) found that large changes in aerosol and small and large ion concentrations occur within a few minutes, thus dispelling any notion of equilibrium conditions existing in natural atmospheres.

Steigerwald (1962) uses his findings to propose qualitative effects of air pollutants on air ions. These effects are: (1) Small ions are very sensitive to particulate contaminants. The introduction of a few thousand condensation nuclei can decrease the small ion density by as much as an order of magnitude. Since city air can contain hundreds of thousands of nuclei, only small concentrations of small ions will exist. (2) The controlling parameter of the condensation nuclei is the total surface area, not the number density. The factor r^2Z is frequently cited as controlling small ion decay ($r=$ nuclei radius, $Z=$ nuclei concentration). (3) Small ion formation is not as important as the condensation nuclei concentration since it is involved to only the $\frac{1}{2}$ power in the equilibrium equation. (4) Large ions will have only one electronic charge. (5) Times from a few seconds for small ions to 30 minutes for large ions are necessary to reestablish equilibrium after an upset. These considerations point out the interdependence of small ion concentration and particulate air pollution. Using these ideas, instruments can and have been made to monitor air pollutants of specific types.

Measurement of Air Ions and Pollutants Using Aspiration Capacitors

Measurements of air ion concentrations, mobilities, or conductivities are usually accomplished with an aspirated capacitor. This device draws a sample of air through a static electric field causing the air ions present to migrate to a measuring electrode. The magnitude of the current determines the concentration of the ions (assuming unit charge for each ion). Development of ion counters has been quite dependent on the state of advancement of electronics because the currents are usually in the range of 10^{-14} to 10^{-12} amperes. For this reason, older measurements used aspirated charged capacitors which lost their charge according to the amount of ions in the air sample.

Devices using the principles of small ion-aerosol particle combination have been constructed which allow one to relate air contamination (of certain forms) to ion concentrations. These instruments generally employed ion generators to give much larger currents than would result from natural ion concentrations. These generated ions are then exposed to aerosols which cause a decline in the ionic concentration depending on the aerosol concentration. Langer and Radnik (1961) employed the above method in an aspiration capacitor to detect particulate concentrations. A commercially available instrument (Maley, 1960) uses the same principle to detect specific gaseous contaminants. Here the gases are first changed to aerosols by suitable chemical reactions. Other instruments which operate to detect aerosol size and charge are described by Hurd and Mullins (1962) and Masters (1953).

A new type of ion counter was built for this investigation, and details of its construction and operation are included in this thesis. This instrument monitored natural ion levels. The concentrations of air pollutants were found to have some degree of correlation to air ion densities. The ion monitor thus has potential as a simple, rugged instrument for detecting air quality.

Further information on aspiration capacitors and ion measurement can be found in Tammet (1970), Israel (1971), Kassner and Yue (1973), Mendenhall and Fraser (1963), Tang and Castleman (1972), Hicks and Beckett (1957), Masters (1953), and Steigerwald (1962). Measurements of Aitken nuclei can be found in Pollak (1959).

Air Ion Studies

Investigators have done voluminous work on air ions, but very little has been done relating air ions to pollution. In the first third of this century and after World War II, much attention was focused on the relation of air ions to various biological, physiological, and psychological effects. Information here is at best inconsistent. During the same period, there existed some interest in aspects of using air ions to more closely approximate outdoor air in air conditioning experiments. More information on these two topics can be found in Silverman and Kornblueh (1957), Krueger and Smith (1959), Yaglou, Benjamin, and Choate (1931), Yaglou, Brandt, and Benjamin (1931), Yaglou and Brandt (1933), Yaglou (1961), Brandt (1933), Kenline (1966), Beckett (1954), Beckett (1959), Murphy (1951), Hicks and Beckett (1957), Hicks (1956), Gordieyeff (1956), Kornblueh (1960), and Minehart, David, and Kornblueh (1958).

Since the beginning of ion measurements there has been evidence that sources of fine particle air pollution (smoke, etc.) have greatly affected small ion concentrations. Various authors, including Pollock (1915), Parkinson (1948), and Wait and Parkinson (1951) have reported large variations in the intermediate ion populations which are connected to changes in wind direction. Apparently the various winds brought air-borne pollution to their measuring sites. Practically all recent investigations of air ion levels have taken into consideration the influence of urban areas. Only a few investigators have been concerned directly with the effects of air pollution on air ions.

Phillips, Allee, Pales and Woessner (1955) studied the rise in conductivity and densities of a mass of air (some 3,000 m^3) as the air was continuously cleaned by an electrostatic precipitator. They found that the negative conductivity increases more than the positive conductivity due to the inherently higher mobility of the negative ions. The concentrations of ions of both polarities equalized since the chamber used was metal and no electric field existed inside (hence no electrode effect).

Steigerwald (1962) investigated the effects of air contaminants on air ions. His findings included: intermediate ions were not generally found in rural areas; negative and positive large ions were equal in concentration in both urban and rural air; a decreased small ion and an increased intermediate ion and large ion concentration in urban air as opposed to rural air; little effect of relative humidity on ions; little effect of carbon dioxide and some effect of sulfur dioxide on small ions; and a strong correlation of automobile exhaust with large ion concentration. He concluded that auto exhaust "appears to be the dominant factor in the alteration of natural air levels in urban location". He also set forth a partial objective of this thesis ".... the study of selected air ion mobilities, perhaps in conjunction with other air measurements, may prove valuable in the investigation of specific types of air contaminants or special atmosperes".

Steigerwald's finding of the correlation of large ions to auto exhaust was supported by the findings of Brasefield (1959) and Westermark (1961), both of whom found large concentrations of ions of either sign in the exhaust of combustion engines.

Beckett (1959) found that the small ion concentration decreased and the intermediate ion concentration increased during rush hours. He found great decreases in the intermediate ion concentration on weekends and in mountain air.

Gunn (1964), on a cruise over the North Atlantic ocean, measured the small ion conductivity and reported a general decline from previous measurements made aboard the *Carnegie*. He attributed this decline to an increase in air pollution (mainly aerosol particles).

During the 1967 global expedition of the *Oceanographer*, Cobb and

Wells (1970) made conductivity measurements in the North Atlantic and South Pacific. They found that there has been a decline of some 20% in the conductivity of the air over the Noth Atlantic during the last 60 years. Cobb and Wells figured this to be equivalent to a doubling of the aerosol concentration. Most of the aerosol, they felt, was due to man-made pollution.

In 1972, Sharp found a relation between air pollution and small ion concentration and the germination of fungi spores. The former finding confirms Steigerwald's prediction (1962) that small ion concentrations would be a more sensitive indicator of pollution than the intermediate or large ions.

Cobb (1973) made conductivity measurements from Mauna Loa, Hawaii, and from ocean vessels and found that aerosol levels are not increasing in most oceanic areas. He found high concentrations of aerosols off the east coasts of the United States and Japan, suggesting that the aerosol is the result of combustion processes. He concluded that cleaner technology will reduce the levels of the anthropogenic aerosols and that no significant global climate changes will take place.

An idea that some atmospheric gaseous contaminants could affect the concentration of the condensation nuclei and in turn the concentration of small ions was put forth by Junge (1951). Steigerwald (1962) reported that Deleanu (1958) suggested and experimented with the use of ion measurements as an index of air quality. Deleanu, however, made no measurements of air contaminants in his study.

The ideas of the gaseous contaminants of the air affecting the density of the condensation nuclei can perhaps be better appreciated when one investigates the composition of such nuclei. Israel (1971) states:

> "In atmospheric air, there must always be a sufficient number of starting points for condensation (the abovementioned condensation nuclei), since otherwise normal cloud formation cannot be explained. Theory and experience have proved that these condensation nuclei are suspensions, the radius of which lies between 10^{-8} to 10^{-5} cm. It was also found that the suspensions in the atmosphere are largely composed of common salt or sea-salt solutions on one hand and nitrogenous gases or H_2SO_4 on the other."

From this information, and from the fact that much air pollution consists of SO_2 and nitrogen oxides, one can see a direct connection of air pollutants to aerosol density. Since combustion processes account for the majority of contaminants entering the atmosphere, one can infer that sufficient water vapor exists with the emitted SO_2 or nitrogen oxides to create micro-solutions suspended in the air. This point, however, remains to be proven. There exists another phenomenon which might tie Steigerwald's contention (1962) of a shift in the mobilities of ions (especially the small ions) to Junge's proposal (1951) of gaseous contaminants influencing the aerosol concentration. That phenomenon is clustering.

Clustering is a process where molecules of atmospheric gases attach themselves to an already existing ion. Recently there has been considerable effort in this field and general findings have shown that SO_2, nitrogen oxides, and water vapor play very important roles in clustering about small ions. The cluster ions may have mobilities as much as an order of magnitude less than the original ion. This points to a potential air quality monitor by measuring a shift in small ion mobilities, or an increase or decrease of certain specific mobilities. Such a concept is the basis of measurements performed in this investigation. For more information on clustering processes, see Mohnen (1970), Ferguson (1971, 1971, 1973), Fehsenfeld and Ferguson (1972), Keller, Beyer, and Colonna-Romano (1973), Keller and Niles (1971), Niles, Heimerl, Keller and Puckett (1972), Hoffert and Stewart (1973), Thurman and Kassner (1973), Castleman (1972), Tang, Munkelwitz, and Castleman (1971), Castleman and Tang (1971, 1972), Castleman, Tang and Munkelwitz (1971), Tang and Castleman (1972), and Castleman, Munkelwitz, and Manowitz (1973).

Experimental Technique and Apparatus

Introduction

For this investigation, an ion mobility chamber with coaxial-conical geometry was constructed. Previous measurements have been made by using parallel-plate or cylindrical aspirated capacitors. In order to measure the ion mobility spectrum, one needs to know that laminar flow exists inside the capacitor and that the velocity profile is the same along its entire length. Obviously, these requirements are hard to meet using parallel plates or cylindrical geometry. If the Reynold's number is below the critical value, laminar flow exists, and laminar boundary layers develop along the walls which eventually meet to form the usual parabolic velocity profile found in long parallel sections. For the turbulent flow, the boundary layer is also turbulent and somewhere downstream the entire flow is turbulant. A changing velocity profile is not taken into consideration in the equations for ionic current. Very low velocities in the chamber are not possible since a space charge will develop, not to mention ionic loss by diffusion to the chamber walls. This same diffusion prohibits establishment of a parabolic profile and subsequent measurement due to the necessarily long time of flow through the chamber intake system. Since boundary layers are present in all real fluids, their elimination is impossible. However, they can be suppressed in a converging channel design and thus maintain a very constant velocity profile. Hoppel (1963) discussed boundary layers in ion chambers and found the converging channel very promising as the flow will approach potential (nonviscous) flow at high Reynold's numbers. In 1970, Hoppel proposed that a chamber of coaxial-conical geometry would offer the advantages of the converging channel and the cylindrical designs. The velocity profile would remain constant yet there would not be fringing electrical fields or edge effects.

Serious problems occur in ion mobility chambers if turbulence develops inside. Turbulence can occur from small perturbations along the boundaries, from the growth of vortices along the entrance, and from the transport of outside turbulence into the chamber. Hoppel (1970) discussed these problems and pointed out that smooth boundaries and the converging channel largely eliminate the first two causes. The last cause is more difficult to eliminate. Usually the solution is to install a settling chamber at the mouth of the instrument. This is merely a structure to break the outside flow into smaller eddies. The problem induced is that the settling chambers provide large surface areas for ionic diffusion to take place. A compromise of area versus reduction of turbulence can be made and the resulting loss of ions can be calculated.

Analysis of the Ion Mobility Spectrum Analyzer

A cross-sectional diagram of the Ion Mobility Spectrum Analyzer (IMSA) used in this investigation can be found in Figure II. This chamber with little modification could be used as an ion counter, a conductivity chamber, or a mobility chamber. The following analysis of this chamber parallels that of Hoppel (1970). In order to make a measurement, atmospheric air is drawn into the chamber by a fan. An electric field is established between the outer cylinder, of radius R_1, and the inner diverging cone. The electric field is:

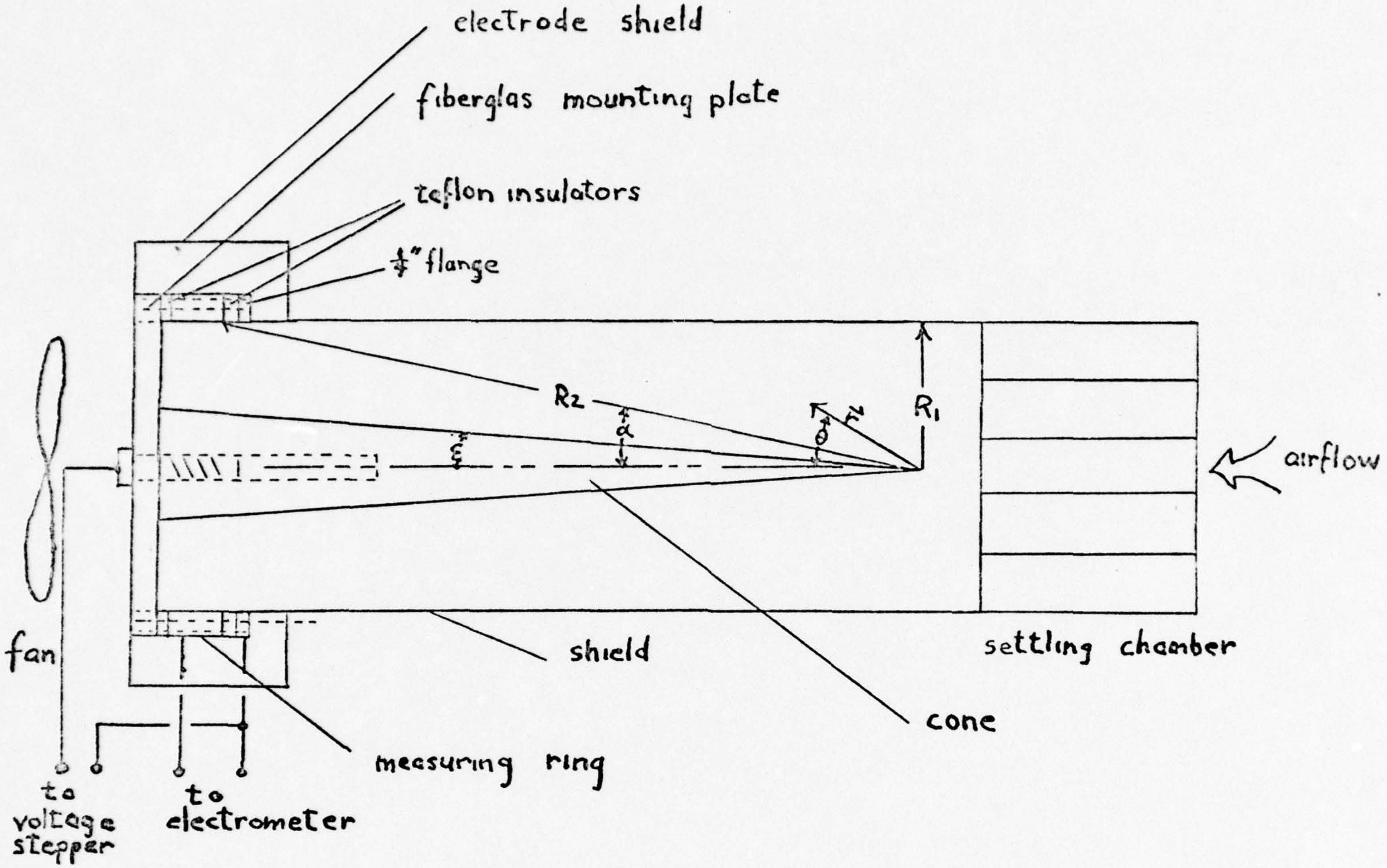

FIGURE II: SCHEMATIC DIAGRAM OF IMSA

$$E = -\frac{V_0\,\hat{\theta}}{r\,(\sin\theta)\,(\log\tan{}^{\pi}/4 - \log\tan{}^{\epsilon}/2)} \qquad (1)$$

where V_0 is the voltage across the cylinder and cone, $\hat{\theta}$ is the unit vector in the direction of the polar angle θ, r is the radial distance, and ϵ is the angle of divergence of the inner cone. The ion will be subject to two velocity components, one a fluid velocity component, $v(r,\theta)$ in the positive radial direction, and an electrical field component, kE, where E is the electric field and k the ionic mobility. The differential equation of the ion path is:

$$\frac{d\theta}{dr} = \frac{kV}{\sin\theta\,(\log\tan{}^{\pi}/4 - \log\tan{}^{\epsilon}/2)\,r^2}\;\frac{1}{v(r,\theta)} \qquad (2)$$

One can define a critical mobility, the mobility an ion must possess if it enters a $r=0$, $\theta=0$, and is collected at $r=R_2$, $\theta=\alpha$ (the point at the far end of the outer cylinder). Using the above differential equation, one can solve the equation of ion path. A simplified solution can be obtained by using the method of Landau and Lifshitz (1959) where:

$$v\,(r,\theta) = f(\theta)r^2 \qquad (3)$$

Equation (2) now becomes:

$$f(\theta)\sin\theta\,d\theta = \frac{kV}{(\log\tan{}^{\pi}/4 - \log\tan{}^{\epsilon}/2)}\;\frac{dr}{r^4} \qquad (4)$$

Equation (4) can be solved exactly. However, if it is expressed in the form:

$$\frac{kV}{(\log \tan \pi/4 - \log \tan \epsilon/2)} \int_0^{R_1} \frac{dr}{r^4} = \int_\varepsilon^{\Pi/2} f(\theta) \sin \theta \, d\theta =$$

$$\int_\varepsilon^{\Pi/2} v(r,\theta) \frac{1}{r^2} \sin \theta \, d\theta \qquad (5)$$

and rewritten as:

$$\frac{kV}{(\log \tan \pi/4 - \log \tan \epsilon/2)} \int_0^{R_1} dr =$$

$$\int_\varepsilon^{\Pi/2} v(r,\theta) \, r^2 \sin \theta \, d\theta \qquad (6)$$

the last integral can be recognized as the volume rate of air flow, Φ, divided by Π. The critical mobility is:

$$k_c = \frac{\Phi}{4 \Pi VC}$$

where

$$C = \frac{R_1}{4 \, (\log \tan \pi/4 - \log \tan \epsilon/2)} \qquad (7)$$

If we let the number of ions in the mobility interval dk be denoted as f(k)dk, then the current to the electrode resulting from ions with mobilities greater than the critical mobility will be:

$$I_{k>k_c} = \Phi e \int_{k_c}^{\infty} f(k)\,dk \qquad (8)$$

An ion of mobility less than the critical mobility will be captured only if it enters the chamber at a point R_i and $\theta = \pi/2$, where R_i must be less than R_1. Equation (5) becomes:

$$\frac{\Pi k_c V}{(\log \tan \pi/4 - \log \tan \epsilon/2)} \int_{R_i}^{R_1} dr = \Phi_j \qquad (9)$$

where Φ_j is the volume rate of flow between R_i and R_1. The current resulting from the ions of mobility k_j is:

$$I_j = n_j e \, \Phi_j = \frac{n_j e \Pi V k_j \, (R_1 - R_i)}{(\log \tan \pi/4 - \log \tan \epsilon/2)} \qquad (10)$$

where n_j is the density of ions with mobility k_j. The current due to all ions of mobility less than the critical mobility is:

$$I_{k<k_c} = \frac{eV \, (R_1 - R_i)}{(\log \tan \pi/4 - \log \tan \epsilon/2)} \sum n_j k_j =$$

$$= \frac{e \Phi}{k_c} \int_0^{k_c} k f(k) \, dk \qquad (11)$$

The total current is therefore:

$$I = \Phi e \left[\int_{k_c}^{\infty} f(k)\, dk + 1/k_c \int_0^{k_c} k\, f(k)\, dk \right] \qquad (12)$$

Equation (12) is a standard form for the expression of the current in parallel plate, cylindrical, converging channel, and coaxial-conical ion chambers. Only the expression of k_c changes. In a divided electrode chamber, one electrode has an insulated segment which permits the separation of ions into distinct mobility intervals. In the case of the coaxial-conical chambers the insulated segment is a small ring on the outside electrode. With this design, the electrical capacitance of the portion of the outer electrode (shield) in front of the small ring (ring) is designated as c_1. The capacitance of the ring to the inner electrode (cone) is c_2. The critical mobility of the chamber portion in front of the ring, associated with c_1 is:

$$k_c = \frac{\Phi}{4 \Pi c_1 V} \qquad (13)$$

and the critical mobility of the front and small rear portions of the chamber associated with $c_1 + c_2$ is:

$$k_d = \frac{\Phi}{4 \Pi (c_1 + c_2)\, V} \qquad (14)$$

where k_c and k_d are in $cm^2\ volt^{-1}\ sec^{-1}$ if Φ is in $cm^3\ sec^{-1}$, V is in volts, and c_1 and c_2 are in cm. Hoppel and Kraakevik (1965) give equations for finding a mobility distribution from a divided electrode chamber. An average mobility distribution can be defined:

$$\overline{f(k)} = \left[\int_{k_d}^{k_c} f(k)\, dk\right] \Big/ \int_{k_d}^{k_c} dk = \frac{1}{4\Pi e c_1 (k_c - k_d)} \left[\frac{d\ I/V}{dk_c}\right] \qquad (15)$$

The ratio $k_d/k_c = c_1/c_1+c_2$ determines the "resolution" of the chamber. As the ratio approaches unity, $\overline{f(k)}$ approaches the true distribution, $f(k)$. The mobility distribution can be calculated from equation (15). Hoppel (1970) uses a point to point differentiation to draw the mobility distribution since equation (15) is dependent upon the slope of I/V. Numerically,

$$\overline{f_i(k_i)} = \frac{c_1 + c_2}{4\Pi e c_1 c_2 (k_{c_i}\, k_{c(i-1)})^{\frac{1}{2}}} \left[\frac{(I/V)_i - (I/V)_{i-1}}{k_{c_i} - k_{c(i-1)}}\right] \qquad (16)$$

where $\overline{f_i(k_i)}$ is centered about $k_i = (\overline{k_i}\ \overline{k_{i-1}})^{\frac{1}{2}}$ and $\overline{k_i} = (k_{c_i}\, k_{d_i})^{\frac{1}{2}}$.

The geometric mean centers $\overline{f(k)}$ about the correct mobility in an analysis of ions with a single mobility. The ion density and conductivity can be found from the distribution function:

$$n = \sum_i \overline{f_i(k_i)}\ (\overline{k_i} - \overline{k}_{i-1})$$

and

$$\Lambda = e \sum_i k_i\, \overline{f_i(k_i)}\ \overline{(k_i - k_{i-1})}.$$

Description of Apparatus

Central to the experiment is the Ion Mobility Spectrum Analyzer (IMSA). This device consists of an aluminum cone surrounded by a concentrically mounted aluminum tube.. The outer aluminum tube is divided into two parts, the fore part (and much larger section) as the shield and the measuring ring.

The central cone, which forms the inner electrode, is mounted on a piece of 1/2" thick fiberglass attached to the outer tube via teflon sleeves and plates. The measuring ring is also teflon insulated. Both the inner cone and the measuring ring are bolted to the outer tube with common 1/4" steel bolts. The teflon sleeves and plates serve to electrically insulate the inner cone and the measuring ring from the outer tube. Teflon is necessary as resistances must be on the order of 10^{13} to 10^{14} ohms-m to match that of air. This form of construction has several advantages from an engineering standpoint. First, the desired coaxial-conical geometry is obtained without the necessity of a large and expensive outer conical shape. The inner cone forms the converging channel and the outer cylinder is easily and inexpensively obtained. Aluminum tubing of this size (I.D. 5 1/2"; wall thickness 1/16") is sufficiently rigid to support the flanges, insulating plates, measuring ring, inner cone and necessary ducting. The aluminum provides a conductive surface when treated by a chemical process known as irriditing. All parts of the apparatus are irridite-treated.

At the entrance to the IMSA is a settling chamber to reduce entering turbulence to allow laminar flow through the device. This is relatively important since the flow velocities of 50-100 cm/sec are readily altered by wind gusts.

Air flow through the IMSA is provided by a small electronic instrument cooling fan (Muffin Fan, Woodstock, N.Y.). The original air flow was much too great, but speed control is provided by a variable transformer. Measurements show that the fan motor tends to lock into the current frequency thus maintaining very constant air flows. The original housing for the fan was removed and the motor and fan installed in a special mounting in the ducting following the IMSA. The ducting is primarily composed of a 6" PVC sewer pipe, with a 90° elbow and some interconnecting pieces of the 5 1/2" O.D. aluminum tubing. Wide adhesive tape was used to seal all joints. The exit for the air is through a diffuser tube made of "rubberized horsehair" packaging material. This helps lessen the effects of external winds. Table V lists the physical, electrical, and ionic characteristics of the IMSA.

The IMSA and all attendant ducting and electrical apparatus are housed in a specially constructed cube to protect the equipment from the weather, electrical noise, solar heating, and temperature variations, and to put the intake of the IMSA some four feet above ground to prevent dust and other low-level particles from entering. The cube is constructed from exterior plywood and lined with 3 1/2" thick fiberglass insulation. Both the inside and outside of the walls are covered with aluminized mylar to provide reflective, electrical, and weather barriers. The fiberglass insulation is used to lessen the variance in temperature which affects the electronic equipment inside. The cube performed admirably in protecting the various equipment from some 20 inches of rain during the time of the experiment.

The heart of the IMSA is the electronic package which allows the minute currents encountered to be amplified to a reasonable level. This package consists of an operational amplifier from Analog Devices, no. 311J. This op-amp, in the arrangement used, will give an output on the recorder used of 50, 100, or 200 femtoamps per inch. The amplifier is quite capable of being much more sensitive, but an increased

length of mobility chamber, excluding measuring ring	14"
overall length of chamber including measuring ring and settling chamber	19 1/8"
width of measuring ring	1"
angle of convergence,	3.1°, .058 rad.
inside diameter of shield (outer cylinder)	5 3/8"
length of settling chamber	4"
velocity of air flow	54 cm/sec
Reynold's number	4500
volumetric air flow	8.1×10^3 cm^3/sec
capacitance of shield and cone, c_1	1.7×10^{-11} fd.
capacitance of measuring ring and cone, c_2	2.5×10^{-12} fd.
resolution of chamber, c_1/ c_1+c_2	.87

TABLE V: PHYSICAL AND ELECTRICAL CHARACTERISTICS OF IMSA

Plate Voltages, V	Mobility Intervals, cm^2/V sec	Mobility Interval Width
Run 7		
± 360	.10 - .11	.01
± 305	.12 - .13	.01
± 239	.15 - .16	.01
± 174	.22 - .23	.01
± 119	.30 - .35	.05
± 78.5 **	.46 - .53	.07
Run 8		
± 90.0	.40 - .46	.06
± 76.3	.46 - .53	.07
± 59.8	.58 - .68	.10
± 43.5	.83 - .94	.11
± 29.5	1.2 - 1.4	.20
± 19.6 **	1.8 - 2.2	.40

TABLE V: IONIC CHARECTERISTICS OF IMSA

** These mobility intervals were not sampled on runs 7 and 8 to provide a zero level determination. They were sampled on runs 5 and 6.

sensitivity only brings increased noise problems. The 200 fA range was used throughout the experiment. Voltage gain of this circuit is set at 10, while current gain is better than 10^{10}! Deposited carbon resistors are used as they were the only type available at the time of construction. The major disadvantage of these resistors is their long-term instability. However, since the experiments were done only over a period of a few days, the resistors proved quite capable. The output from this electrometer circuit is fed into a Texas Instrument dual channel recorder.

The voltage used to create the electric field of the IMSA is generated from a series of 90 volt bateries whose output voltage is tapped from a resistor ladder to give voltages used. The circuitry to put this battery voltage on the IMSA and switch it to change polarity and/or voltage was constructed in the lab. Both the electrometer and voltage stepper functioned without problems. The output from the voltage stepper is shown on the other channel of the above-mentioned recorder. Schematics of the circuitry appear in Figures III, IV, and V.

In order to minimize the variations in output with temperature of the electrometer circuit, a temperature compensating circuit is used. To further stabilize the performance of the electrometer the entire circuit is housed in a styrofoam picnic cooler with several plastic bottles filled with water. This arrangement provides for insulation and a large thermal inertial mass to dampen temperature changes. In this manner, the electrometer experienced only a 5° C temperture variation over a 24-hour period, a variation much smaller than the 25° C variations we recorded at similar rooftop locations.

The ion loss by diffusion to the walls of the settling chamber

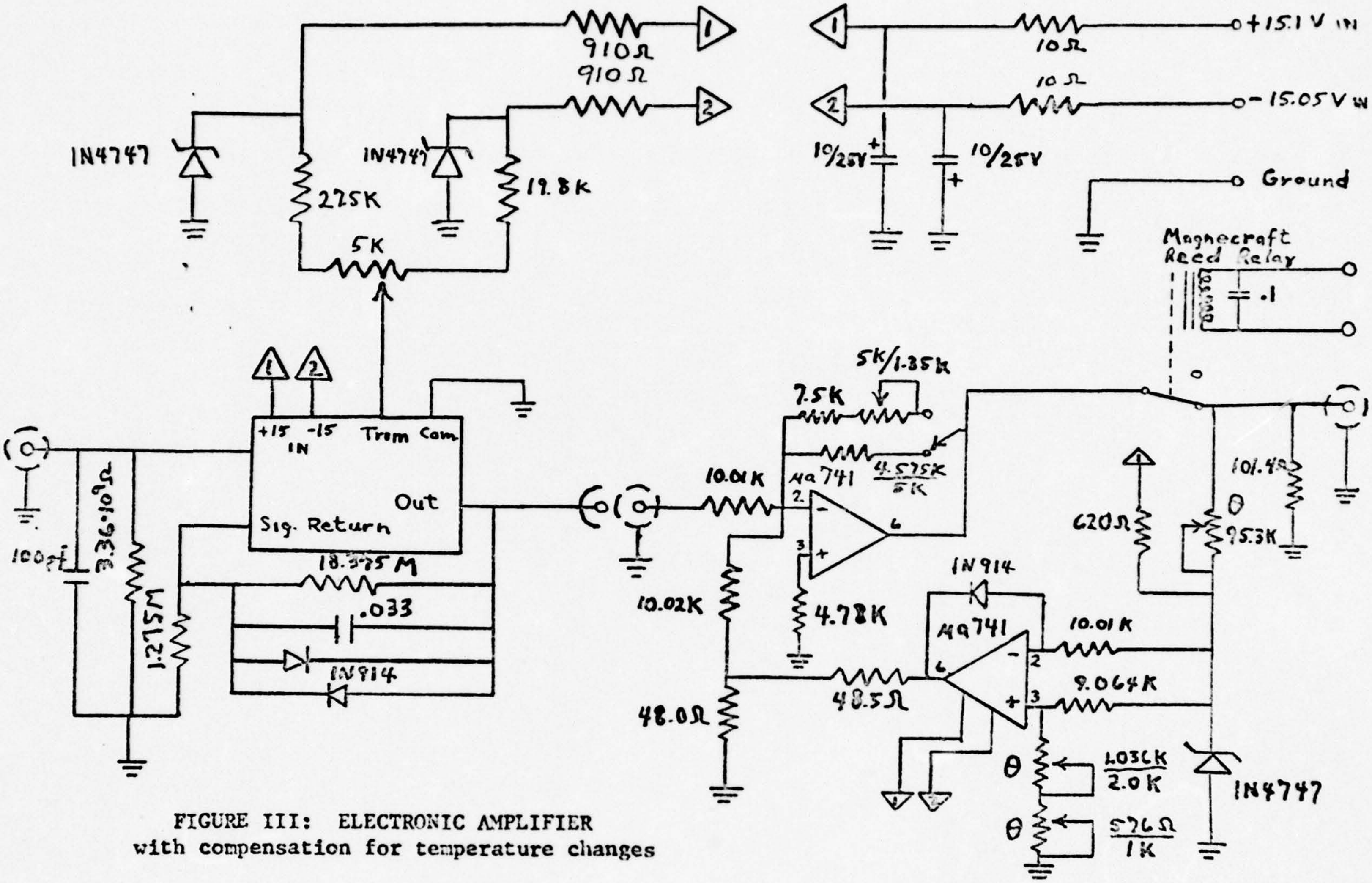

FIGURE III: ELECTRONIC AMPLIFIER
with compensation for temperature changes

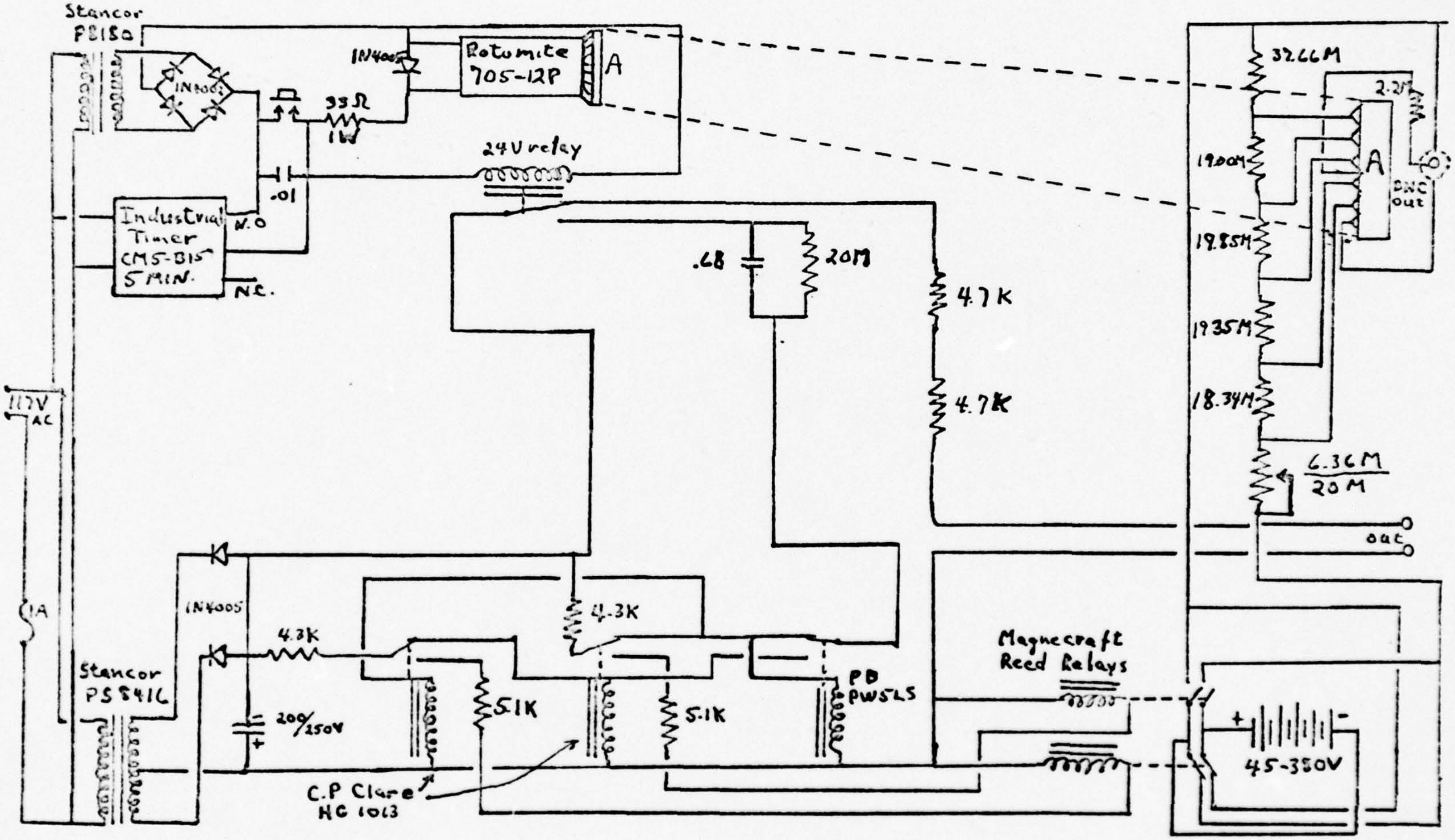

FIGURE IV: VOLTAGE STEPPER

*The pot is set with a ratio of 928.7 to 104.5.

$$\text{So, } V_g = .000010105 \text{ V/V}$$
$$= 1.0105 \times 10^{-5} \text{ V/V}$$

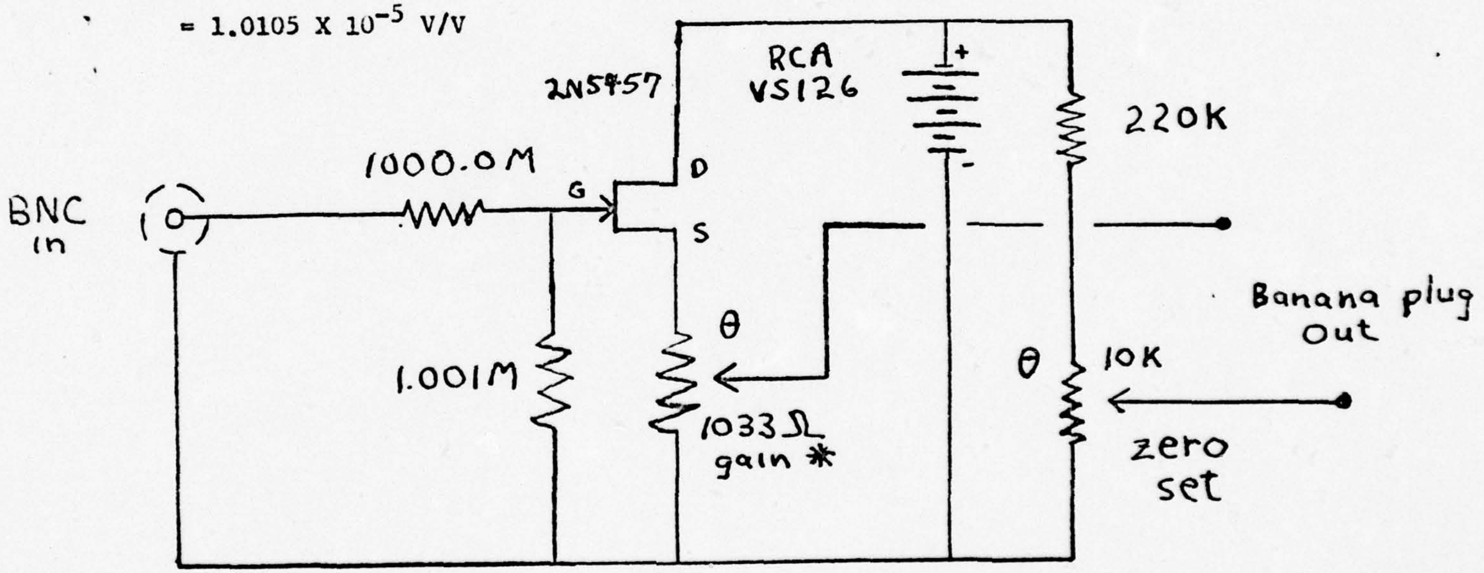

FIGURE V: VOLTAGE ATTENUATOR
with high input impedance

and the intake pipe was estimated by two methods. Rich (1959) gives a method of estimation, which calculated for ions of mobility of 2 $cm^2/Vsec$, shows a loss of less than one per cent of the incoming ions. Cobb (1968) did an investigation of ion losses in ion chamber intake systems and interpolation from his data shows little, if any, ion loss.

Experimental Technique

All mobilities tested for were in the range which Israel (1971) defines as small to small intermediate ions. This range was chosen in order to prevent the establishment of extremely high electric fields, which, it is felt, could easily alter ion structure. Higher mobilities were to be observed, but an error in preliminary calculations prevented doing this. The mobility intervals were set as a matter of convenience in design of the voltage stepping circuitry. This mobility range should show high sensitivity to cluster formation and some sensitivity to particulate matter. (The mobilities of cluster ions measured in laboratories are on the order of 2 cm^2/V sec to 0.5 cm^2/V sec. Particulate matter will yield ions with mobilities orders of magnitude lower.) There was no overlap in the mobility intervals. The mobility interval of 0.46 to 0.53 cm^2/V sec was not sampled twice as the voltage stepping apparatus had provisions for only six distinct voltages at one time. This meant that two runs were made, one with the higher voltages (360V - 78.5V) and another with the lower voltages (90V - 19.6V). In all, a total of four complete runs were made, the first and fourth were the 90-19.6V range and the second and third were the 360-78.5V range. Each run took about 48 hours, in which time some 40-44 separate measurements of each mobility interval were made. The measuring period for each interval was some five minutes. Response time of the electronic circuitry was about 20 sec, hence most of the five minute period was used to record the ion density. With the five minute sampling time, all six intervals (five in the latter two runs) were measured for ions of both polarities each hour. This proved to be a very workable system as the air contaminant levels were reported hourly. It is accepted practice in meteorological measurements to sample for at least three minutes, which is a mean mixing time in a distinct air cell, and to report hourly variations in the measurement, as one hour is a mean time for air cell movement past the sampling station. Forty or more points were desired in order to establish a large sampling space where a statistical "t" distribution would be valid. The "t" distribution is used as a basis for multiple regression analyses. The experimental data were correlated to air pollutant levels from standard measuring devices. In this manner, the potential of the IMSA could be evaluated by simple correlation coefficients between single ion mobilities and air pollutant measurements and by multiple correlation coefficients between single ion mobilities and all pollutants. The former correlations could demonstrate that certain pollutants form ions of a characteristic mobility or mobilitites. The latter measurements could show the usefulness of the IMSA as an indicator of general air quality. A computer program was used to perform the regression analysis. The program was taken from the Biomedical Research Computer Programs (Health Sciences Computing Faculty, University of California at Berkeley).

The air pollutant measurements were taken from three air quality monitoring stations operated by the Houston Department of Public Health.

The IMSA was installed on the roof of the Public Health building in order to sample the same air as the monitoring station located in the penthouse of the same building. There are no strong sources of pollution nearby and convective winds mix the air quite well, hence there was little possibility of the IMSA sampling air that the monitoring station would not also sample. At the time of the investigation, only two of the Health Departments's monitors were operating, those measuring sulfur dioxide and total hydrocarbons. Although only these two pollutants were being measured, it does not mean that the results obtained with the IMSA are not representative. Sulfur dioxide is generally associated with industrial pollutants and is well-known to participate in clustering and to form aerosol particles (Castleman, Tang and Munkelwitz, 1971; Israel, 1971). Total hydrocarbons are generally connected to auto exhausts. Steigerwald (1962) has already found a strong correlation between auto activity and ion densities. These two pollutants can well indicate the major sources of pollution in the urban atmosphere.

Since only two pollutants could be obtained from the air quality monitors at the Public Health Building, it was decided to utilize pollutant levels measured at two other stations in the city for comparison. The first was located in downtown Houston some 3.5 miles from the IMSA station. Pollutants measured here were carbon monoxide, sulfur dioxide, nitrogen dioxide, and total oxidants. It was felt that these measurements could give a good indication of the changes in the same pollutants at the IMSA location since both locations experience similar traffic activity and neither are near strong fixed sources of pollution.

The same reasoning was used in including the measurements from a third station near the Ship Channel area, about 6 miles distant. This latter station is closer to a large petrochemical and industrial complex, which introduces uncertainty about the similarity of results. However, a visual inspection of the results from the three stations implies that although absolute values are different, changes in pollutant levels follow similar trends. This is further confirmed by statements of the station operators who notice similar patterns in all three stations. Houston is rather flat, hence convective winds keep the air below the inversion layers fairly well-mixed. Also the days of the experimental runs were characteristically fair weather days, i.e., sunny, scattered cumulus clouds that disappeared by late morning, a lot of convective winds in the mid-morning and late afternoons, and a low but steady wind that shifted direction frequently during the mid-day and night. The pollutants measured at the third station were sulfur dioxide, total hydrocarbons, ozone, nitrogen dioxide, and total oxidants.

Other investigators have found correlations of ion mobility to relative humidity (Pollock, 1915; Wait, 1935; Erikson, 1927), and there are known changes in mobility with temperature. These two atmospheric parameters were included in the regression analysis to check their effects on ion mobilities. Also included were wind speed and direction since local air contamination can be profoundly affected by either factor. The wind direction was coded by numbering the directions consecutively from north to the west (N=1, E=2, S=3, W=4). This system proved not to be adequate since it should have been scaled so that winds from strong pollution sources would receive the higher values. However, since most of the strong sources were to the southeast, the system was not totally inoperative. A diagram of the locations of the three monitoring station appears in Figure VI.

Data Reduction

The data taken during the experiment was recorded on a dual-channel chart recorder. One channel recorded the ionic currents measured by the IMSA and the other recorded the voltage level and polarity of the measuring electrode. The ionic currents for runs 4 and 5 were read from the charts assuming a constant zero. Visual inspection of these runs showed that the zero point did not remain constant; hence, the later runs, 7 and 8, eliminated the lowest voltage steps and gave a zero line for the instrument at that hour. This proved to be satisfactory and the data from runs 7 and 8 were used in this thesis.

The magnitudes of the ionic currents were established by calibrating the output of the IMSA. The recorder was then set to give a response of 200 femtoamps (200×10^{-15} A) per inch. The chart paper was ruled 10/inch; hence the currents were measured to ± 10 fA. The electrode voltage was clibrated to give about 90 volts per inch or 20 volts per inch depending on the voltage range used in the IMSA. The recorder was synchronized with Central Daylight Savings Time; hence, the data from the IMSA could be directly matched to the Health Department pollutant data.

The trace of the ionic currents was usually quite smooth; however, at times the trace showed continuous variation. This phenomena was attributed to wind gusts which altered the air flow in the instrument. and the ionic mobilities being measured. In these cases, the readings

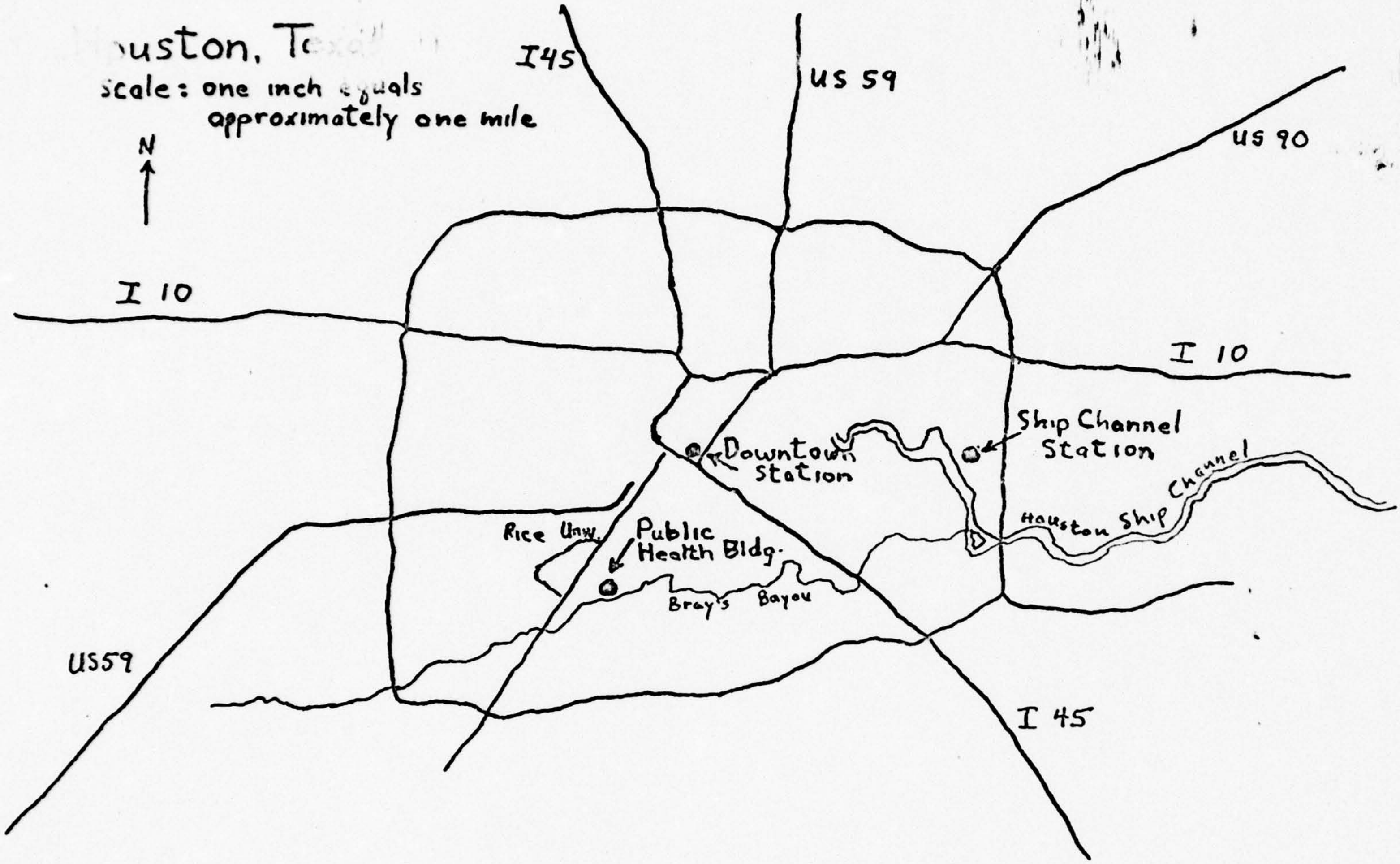

FIGURE VI: LOCATION OF AIR POLLUTION SAMPLING STATIONS were either disregarded or a visual mean found if possible. Some of the pollutant data from the Health Department was incomplete, and in these cases, the measurements were again disregarded.

All data taken, including the pollutant measurements by the City Health Department, were reasonable values. As would be expected in an urban atmosphere, the concentrations of small ions were quite low while the intermediate ions exhibited substantial concentrations. No data on particulate concentration was available,but a substantial aerosol concentration which would explain the observed concentrations of the ions was reported previously. Average ion mobility spectra appear in Figures VII and VIII. These spectra were taken from the average values of all ion concentration measurements made in Runs 7 and 8. The curves were corrected to true ion concentrations by the method of Hoppel (1970).

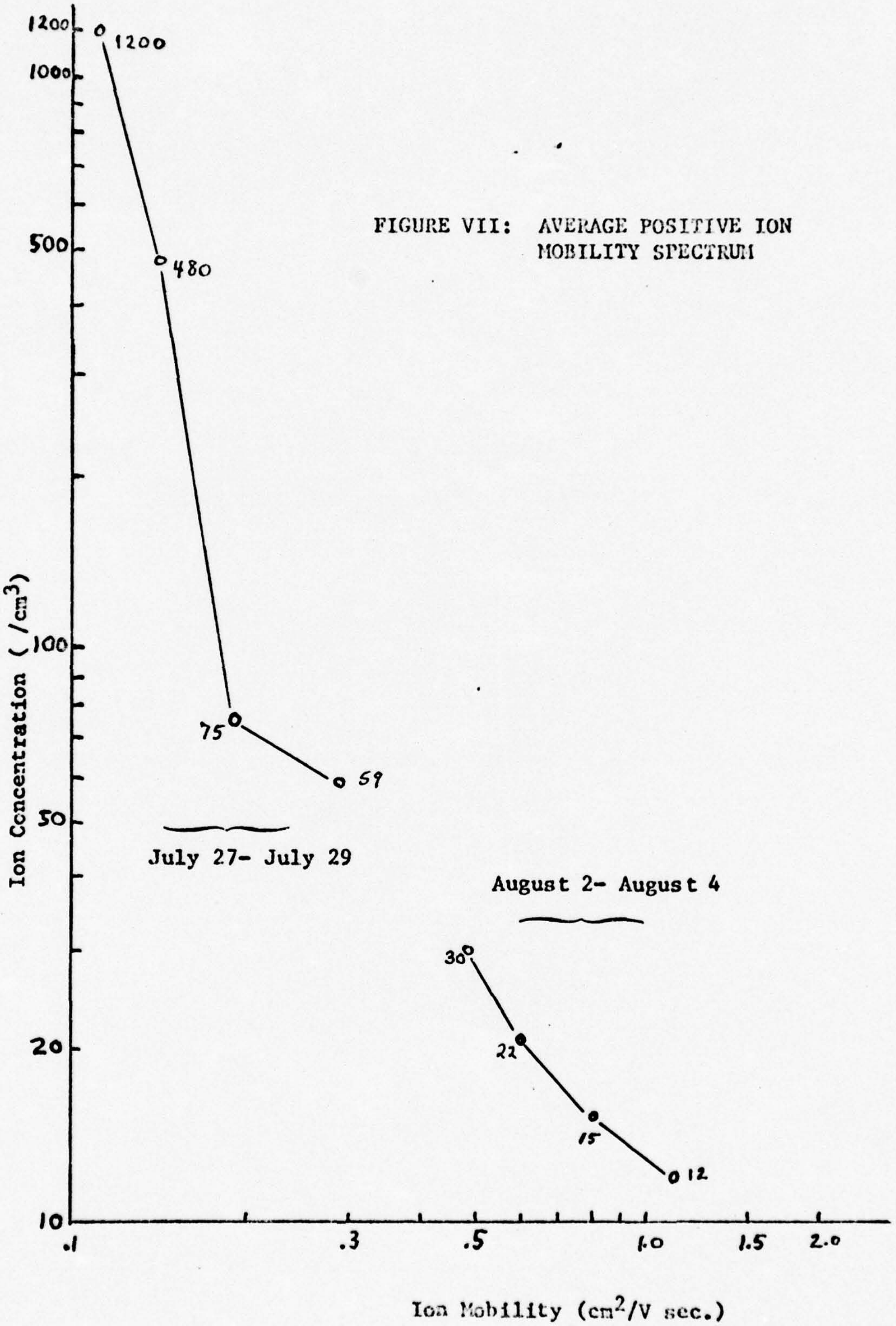

FIGURE VII: AVERAGE POSITIVE ION MOBILITY SPECTRUM

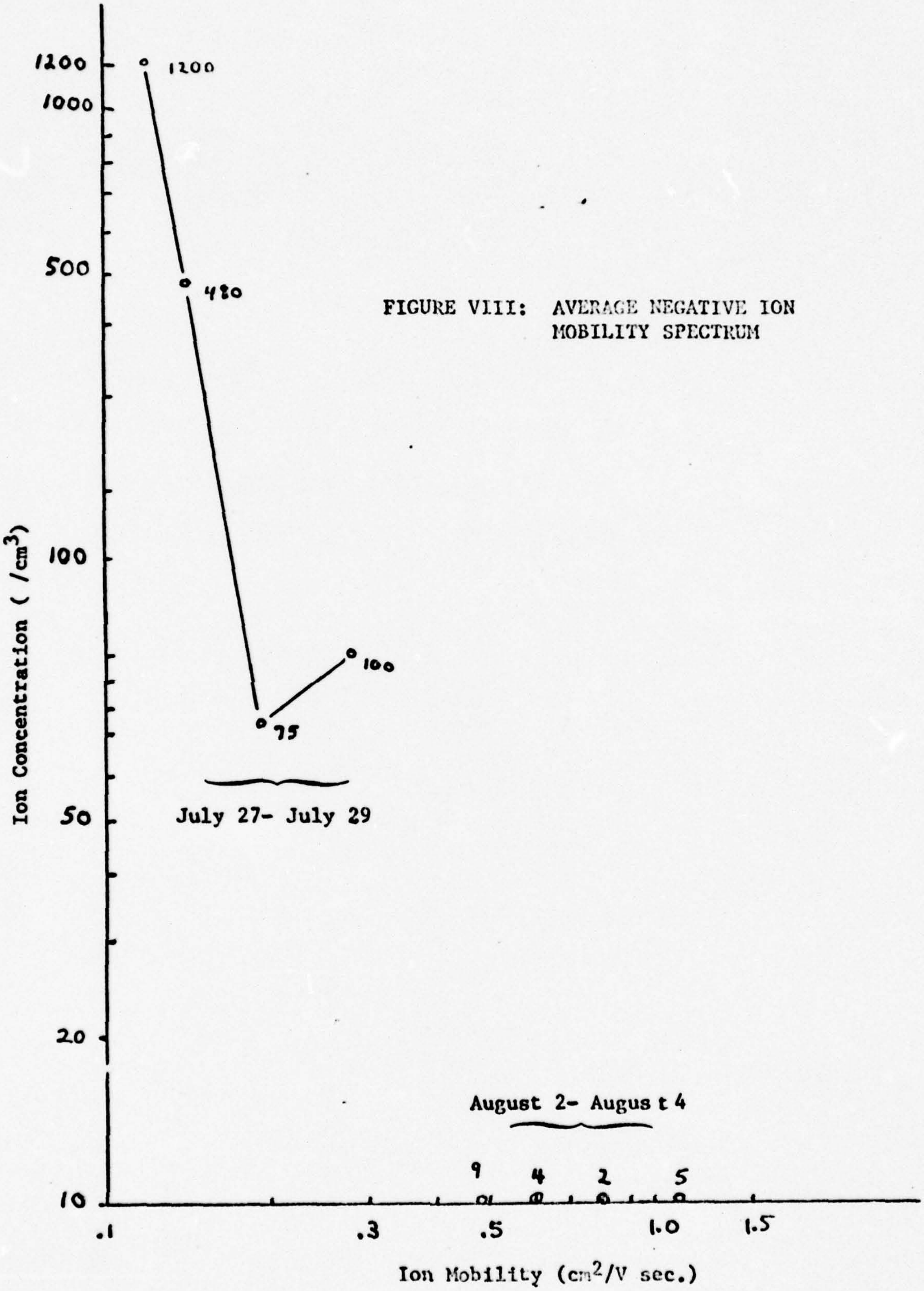

FIGURE VIII: AVERAGE NEGATIVE ION MOBILITY SPECTRUM

Experimental Results

The measurements obtained with the IMSA were correlated to the air quality and meteorological parameters mentioned before. In all, a total of 27 variables with 40 or 41 samples of each were used in the regression model. Samples of the size used tend to preclude the possibility of concluding relationships exist when they really do not. Results of the regression analyses are given in Tables VI and VII.

Steigerwald (1962) states that the most complete information on the effects of air contaminants on air ions could be obtained through the use of a complete air ion spectrum. He finds, however, that complete valid spectra are rather difficult to obtain as natural conditions tend to make the air ion densities fluctuate rapidly, on the order of a few minutes. Since his instrument could not obtain readings for the entire spectrum in that time, he went on to search for effects at specific ion mobilities. Due to much the same reason, this investigation was carried out in the same manner. The instrument used here is much more sensitive that the one used by Steigerwald; hence, it is able to examine the small ions and small intermediate ions, which Steigerwald could not reliably observe. All measurements were made on ambiant air as the purpose of the investigation was to test for the potential of the instrument as an air quality monitor.

The correlation coefficients of the ion mobility intervals to the single atmospheric parameters are in Tables VI and VII. A test for significance (two-tail) at the 1% level determined that a minimum

TABLE VI: CORRELATION COEFFICIENTS - RUN 7

Air Parameter	Mobility Intervals (cm^2/V sec)			
	-(.10-.11)	+(.10-.11)	-(.12-.13)	+(.12-.13)
Public Health Building				
SO_2	-.2402	.1443	-.1460	.1261
Hydrocarbons	-.3710	-.0557	-.1047	-.0899
Temperature	-.0985	-.9781	.8797	-.9828
Relative humidity	.5469	-.2193	.4244	-.2135
Wind speed	-.2840	.2022	-.3523	.2449
Wind direction	-.0260	.0771	-.1523	.0666
Downtown				
CO	-.5214	-.2267	.0951	-.1583
SO_2	-.0885	.1297	-.0416	.0677
Total oxidants	-.6593	.1168	-.2511	.1465
NO_2	-.1990	.0068	.0211	-.0418
Ship Channel				
SO_2	.0688	.1252	-.0193	.1003
Total hydrocarbons	.3157	.4447	-.3272	.4593
O_3	-.7208	.1717	-.2817	.1605
NO_2	-.0557	.1322	-.2460	.1202
Total oxidants	-.6946	.1807	-.3179	.1713
Temperature of electrometer	-.2764	-.0125	-.0752	.0164

SAMPLE SIZE = 41

Minimum values of correlation coefficient to be significant at the 1% level (two-tail) = .41.
Minimum value of correlation coefficient considered acceptable for this investigation = .70.

TABLE VI (cont.): CORRELATION COEFFICIENTS - RUN 7

Air Parameter	Mobility Intervals (cm^2/V sec)			
	-(.15-.16)	(.15-.16)	-(.22-.23)	(.22-.23)
Public Health Building				
SO_2	-.2198	.1563	-.2994	.1795
Hydrocarbons	.0321	-.0851	-.1550	-.0320
Temperature	.9065	-.9772	-.2693	-.9659
Relative humidty	.3399	-.2606	.5105	-.2950
Wind speed	-.2664	-.2238	-.1486	.2302
Wind direction	-.1538	.1258	-.3411	.1035
Downtown				
CO	.2012	-.2343	-.3531	-.1812
SO_2	-.1162	.1050	-.0129	.1038
Total oxidants	-.2542	.1387	-.4674	.1977
NO_2	-.0171	-.0106	-.0968	.0086
Ship Channel				
SO_2	-.1059	.1312	-.0686	.1115
Total hydrocarbons	-.4905	.4855	-.0208	.4658
O_3	-.3040	.1764	-.3431	.2144
NO_2	-.2365	.1368	-.2375	.1559
Total oxidants	-.3346	.2015	-.4323	.2317
Temperature of electrometer	-.1371	-.0139	-.2319	.0352

TABLE VI (cont.): CORRELATION COEFFIENTS - RUN 7

Air	Mobility Intervals (cm^2/ V sec)	
Parameter	-(.30-.35)	(.30-.35)
Public Health Building		
SO_2	-.1128	.0642
Hydrocarbons	.0183	-.0726
Temperature	.9451	-.9344
Relative humidity	.2107	-.2471
Wind speed	-.3538	.3126
Wind direction	.0045	.0717
Downtown		
CO	.2777	-.2755
SO_2	-.0520	.1092
Total oxidants	-.1739	.0849
NO_2	.0511	-.0802
Ship Channel		
SO_2	-.0516	.0088
Total hydrocarbons	-.4041	.4621
O_3	-.2534	.2137
NO_2	-.1395	.1240
Total oxidants	-.2379	.2192
Temperature of electrometer	-.0585	-.0185

TABLE VII: CORRELATION COEFFICIENTS - RUN 8

Air	Mobility Intervals (cm^2/V sec)			
Parameter	-(.40-.46)	(.40-.46)	-(.46-.53)	(.46-.53)
Public Health Building				
SO_2	-.3865	.3054	-.2244	.4448
Hydrocarbons	.2371	-.1416	-.0117	-.1876
Temperature	-.4051	.4078	-.4301	.6565
Relative humidity	.4109	-.4965	.3900	-.6339
Widn speed	.0366	-.1108	.2412	.1228
Wind direction	.2645	-.0120	-.1036	.0314
Downtown				
CO	-.1635	.1630	-.1288	.0663
SO_2	-.1755	.1697	-.1235	.2971
Total oxidants	-.3207	.1678	-.2234	.4124
NO_2	-.0406	.1627	-.1718	-.0288
Ship Channel				
SO_2	-.4394	.1722	-.2709	.5132
Total hydrocarbons	.2913	.2091	-.1425	.1297
O_3	-.4010	.2160	-.1756	.4367
NO_2	-.0378	.5251	-.0435	.1848
Total oxidants	-.1125	-.0625	-.1853	.2468
Temperature of electrometer	-.2212	.4374	-.2527	.3211

Minimum value of correlation coefficient to be significant at the 1% level (two-tail) = .40.

Minimum value of correlation coefficient considered acceptable for this investigation = .70.

TABLE VII (cont.): CORRELATION COEFFICIENTS - RUN 8

Air Parameter	Mobility Intervals (cm^2/V sec) -(.58-.68)	(.58-.68)	-(.83-.94)	(.83-.94)
Public Health Building				
SO_2	-.2295	.4161	-.4347	.4989
Hydrocarbons	.0568	-.3111	.1907	-.3608
Temperature	-.4328	.4503	-.5299	.6458
Relative humidity	.3326	-.4875	.5748	.6769
Wind speed	.1989	-.0199	.1476	.1533
Wind direction	-.1439	.0475	-.0709	.0689
Downtown				
CO	-.0693	.0819	-.0203	.1154
SO_2	-.1270	.2905	-.3320	.3069
Total oxidants	-.2228	.3536	-.3975	.4980
NO_2	-.1853	.1727	-.1441	.0095
Ship Channel				
SO_2	-.2899	.5484	-.5074	.6013
Total hydrocarbons	-.1463	.1161	.0099	.0302
O_3	-.1398	.3752	-.4677	.4933
NO_2	.0769	.1455	-.2079	.2991
Total oxidants	-.1449	.2821	-.1602	.2299
Temperature of electrometer	-.1353	.3332	-.3522	.4292

TABLE VII (cont.): CORRELATION COEFFICIENTS - RUN 8

Air Parameter	Mobility Intervals (cm^2/V sec)	
	-(1.2-1.4)	(1.2-1.4)
Public Health Building		
SO$_2$	-.4247	.5312
Hydrocarbons	.2390	-.2947
Temperature	-.6030	.7644
Relative humidity	.6055	-.7985
Wind speed	-.2048	.0509
Wind direction	-.0993	-.1504
Downtown		
CO	-.1313	.2196
SO$_2$	-.2011	.3563
Total oxidants	-.5364	.5085
NO$_2$	.0031	-.0646
Ship Channel		
SO$_2$	-.4035	.5556
Total hydrocarbons	-.0831	-.2773
O$_3$	-.4696	.5812
NO$_2$	-.1976	.1525
Total oxidants	-.0567	.0362
Temperature of electrometer	-.3802	.2419

value of the correlation coefficient of .41 would be significant. This test of significance shows that one would reject a "good" correlation only one per cent of the time as long as the correlation coefficient was greater than or equal to .41. Another measurement, the coefficient of determination (which is simply the square of the correlation coefficient) shows how much of the variance (or deviation of the measurements) can be explained by the regression. In the case of a correlation coefficient of .41, the coefficient of determination is .168, meaning that the regression variables account for only 17% of the total variance in the regression. This implies that the independent and dependent variables have little correlation or that variables other than those in the regression account for the variance. In order to eliminate dubious cases, the minimum value for this investigation for a correlation coefficient to be considered reasonable was set at .70. This allows for a high degree of correlation and also explains about half of the variance in the regression.

Using this criterion only ten correlations were significant. Of these eight were correlations with temperature, which is quite well-known. There seems to exist a higher degree of temperature correlation to the larger ions than to the smaller ions. This can be explained partly by the mobility interval width. Since the higher mobility intervals were wider, there is less possibility of ions shifting their mobilities out of the interval, especially since the temperature changes were not severe (standard deviation of about 2° C). That some of the correlations were positive and others negative is not easily explained. The mobility of ions should increase with temperature.

Perhaps the negative correlations indicate changes in the structure of the ions.

The two other high correlations were the mobility interval -(.10-.11) cm^2/V sec to ozone measured at the Ship Channel (-.7208) and the interval +(1.2-1.4) cm^2/V sec to the relative humidity at the Public Health building (-.7985). The effects of both water vapor and ozone on air ions are currently being studied in depth. Both contaminants are known to participate in clustering and the winds were favorable for ozone to reach the experimental station. The correlation to ozone could also be due to some other intercorrelated variable. Whatever the case, it would seen that this mobility interval would, in future investigations, be an excellent range to try to determine ozone concentrations. The effects of water vapor are not yet positively known, but this data could lend some knowledge to the structure and to the existence of ions of mobilities +(1.2-1.4) cm^2/V sec. This correlation is unusual in that other investigators have found no correlation of positive ions to humidity (Israel, 1971).

There were a number of other correlations that were quite high and yet not greater than the .70 limit set. For instance, the range -(.10-.11)cm^2/V sec would again be an excellent range to test effects of some fraction or all of the total oxidants concentration (correlation coefficient = -.6946). Many of the other correlations can possibly give some qualitative idea of contaminant effects on air ion densities, and be of use in future investigations of this sort.

The multiple regression coefficients, i.e., those determining the degree of correlation between each mobility interval and all the meteorological and air quality variables, are given in Table VIII. The correlation coefficients and the coefficients of determination are quite high, yet caution must be exercised before deeming that such high correlations imply that the variables used in the regression analyses can be used to determine ionic concentrations and vice versa. The problem is that any two independent variables that are highly correlated to the dependent variable can lead to erroneous results. The cause is inherent to regression analyses in general. For example, in this work both temperature and wind direction were used as independent variables and these both are well correlated to shifts in ionic concentrations and mobilities. These two variables could easily account for the high degree of correlation while the air quality parameters account for very little. This indeed is the case for Table IX shows that temperature, relative humidity, wind speed and wind direction have the highest partial correlation coefficients. (This statistic shows the correlation of the independent variable to the dependent variable after all influence of the other variable is removed.) Since the four above mentioned independent variables can also account for most of the variance in the regression, one cannot draw any conclusions that these high coefficients indicate a high degree of correlation of ionic concentrations to air quality parameters. In order to find if a correlation of air quality to ionic concentration did exist, more work would have to be done where the meteorological variables are excluded. The limits of time prohibited doing this in this investigation. For those who are more familiar with regression anaysis, Table IX lists some of the more significant statistics calculated for this work.

TABLE VIII: MULTIPLE CORRELATION COEFFICIENTS AND COEFFICIENTS OF DETERMINATION

Mobilities	Multiple Correlation Coefficient	Multiple Coefficient of Determination	ANOVA F-value
-(.10-.11)	.8754	.7663	4.91
(.10-.11)	.9858	.9718	51.78
-(.12-.13)	.9628	.9271	19.06
(.12-.13)	.9923	.9846	95.78
-(.15-.16)	.9719	.9447	25.60
(.15-.16)	.9943	.9887	131.10
-(.22-.23)	.8124	.6600	2.9
(.22-.23)	.9864	.9729	53.85
-(.30-.35)	.9821	.9646	40.85
(.30-.35)	.9678	.9367	22.20
-(.40-.46)	.6684	.4468	1.16
(.40-.46)	.7647	.5847	2.02
-(.46-.53)	.7429	.5519	1.77
(.46-.53)	.7846	.6157	2.30
-(.58-.68)	.8162	.6661	2.87
(.58-.68)	.7847	.6158	2.30
-(.83-.94)	.7445	.5543	1.79
(.83-.94)	.8049	.6479	2.64
-(1.2-1.4)	.7759	.6020	2.17
(1.2-1.4)	.9312	.8671	9.28

All F-values are significant (i.e., difference betwee the variance of the regression and the variance within the regression) to the 1% level if the value is 2.94, to the 5% level if 2.12.

TABLE IX: SIGNIFICANT INDEPENDENT VAIABLES

Mobilities	Independent Variable	T Value Std. Error Regression Coefficient	Partial Correlation Coefficient	Cumulative Proportion of Variance
-(.10-.11)	-	-	-	-
(.10-.11)	Temperature	-22.44	.9770	.9164
-(.12-.13)	Temperature	13.17	.9373	.7986
	Relative humidity	2.62	.4719	-
(.12-.13)	Temperature	-29.81	.9868	.9183
-(.15-.16)	Temperature	12.82	.9341	.7603
	Wind speed	2.21	.4121	-
(.15-.16)	Temperature	-33.60	-.9895	.8968
	Relative humidity	-2.78	-.4943	-
-(.22-.23)	Temperature	-3.29	-.5584	-
	Hydrocarbons	2.82	.4994	-
(.22-.23)	Temperature	-22.21	-.9765	.8877
	Relative humidity	-2.22	-.4135	-
-(.30-.35)	Temperature	17.94	.9646	.8825
	Hydrocarbons	-3.03	-.5264	-
	Wind speed	-2.52	-.4579	-
	SO_2 (Dt)	2.28	.4220	-
	NO_2 (SC)	-2.45	-.4474	-
(.30-.35)	Temperature	-13.51	-.9401	.8592
	Total oxidants (Dt)	-2.49	-.4542	-
-(.40-.46)	-	-	-	-
(.40-.46)	-	-	-	-
-(.46-.53)	Wind speed	2.59	.4758	-
(.46-.53)	-	-	-	-

TABLE IX (cont.): SIGNIFICANT INDEPENDENT VARIABLES

Mobilities	Independent Variable	T Value Std. Error Regression Coefficient	Partial Correlation Coefficient	Cumulative Proportion of Variance
-(.58-.68)	Wind direction	2.56	.4712	-
	O_3 (SC)	2.81	.5054	-
	NO_2 (SC)	2.79	.5032	-
(.58-.68)	Temperature	-2.45	-.4552	-
	Relative humidity	-2.15	-.4092	-
	SO_2 (SC)	2.64	.4829	.1438
-(.83-.94)	Wind speed	2.27	.4277	-
(.83-.94)	Relative humidity	-2.17	-.4117	-
	SO_2 (SC)	2.11	-.4019	-
-(1.2-1.4)	-	-	-	-
(1.2-1.4)	Relative humidity	-2.67	-.4859	-
	Wind speed	-3.18	-.5531	-
	Total hydrocarbons (SC)	-3.74	-.6148	-
	SO_2 (PHB)	-2.98	-.5278	.2822

SC = Ship Channel station
PHB = Public Health Building station
Dt = Downtown station

Conclusions

The potential of the IMSA as an instrument capable of measuring air quality remains to be proven. Though firm conclusions cannot be drawn from the results of the investigation, tendencies can perhaps be discerned. Many of the ion concentrations had significant regression statistics with respect to the air quality parameters. Taken as guidelines, these statistics can be used in future work to perhaps find a mobility range or ranges that would accurately follow the concentrations of one or several air pollutants. The usefulness of the IMSA as an indicator of overall air quality awaits a more refined regression analysis technique.

This investigation did show that an IMSA can be built that is substantially simpler, more rugged, and less expensive than present air quality monitoring instruments. If it is found the the IMSA can be used to measure air pollution, then it should prove a valuable instrument due to its inherent simplicity, ease of automation, and lower costs.

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