

DETERMINATION OF THE TIME VARIATIONS  
OF LEAD, CADMIUM, COPPER, AND ZINC CONCENTRATION  
IN AEROSOLS BY SQUARE-WAVE POLAROGRAPHY

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## SUMMARY

The subject of this investigation has been the application of square-wave polarography, in particular the anodic stripping mode, to the determination of the time variations of the lead, cadmium, copper, and zinc concentration in aerosols. One-hour and three-hour average samples of particulate matter were obtained at a rate of 17 liters per minute and 7 liters per minute, respectively, on Whatman 542 and 41 cellulose fiber filters with an A.I.S.I. tape sampler. The sample spots were analyzed for the metals after extraction (which combined the use of 0.1M  $\text{HNO}_3$  as the eluting reagent with ultrasonic agitation), followed by neutralization with ammonium hydroxide and dilution with ammonium citrate buffer at pH 3. Results indicated that the average hourly concentration of the metals fell within the following ranges (in nanograms per cubic meter): 0 to 322 for copper, 0 to 1710 for lead, 0 to 72 for cadmium, and 0 to 372 for zinc. The hourly concentration pattern was different for each of the metals. The lead pattern, and to some extent that of cadmium could be related to traffic; other sources are suggested for the time variations in the concentration of copper and zinc. Metal patterns between week days and weekends were also different for each metal.

Experiments performed with the Whatman hardened ashless grade filters (Whatman 540, 541, and 542) indicated that improvement of the analytical method was possible by using these filters for air sampling in place of the Whatman 41 filter. Although the latter filter has

adequate background levels of copper, lead, and cadmium, its zinc contribution is high (equivalent to 89 nanograms per cubic meter for a one-hour sample) and quite variable. On the other hand, the former filters not only provide an extremely small contribution to the background of all metals studied, but additionally (the Whatman 542 and 540) seem to increase the collection efficiency of aerosol particles in the microgram and submicrogram size range.

The use of sulfosalicylic acid for the electrochemical masking of iron (III) was also examined. It was found that when the supporting electrolyte was made 0.1 percent in sulfosalicylic acid, iron (III) concentrations higher than one ppm did not interfere with the determination of Cu, Pb, Cd, and Zn.

## CHAPTER I

### GENERAL CONSIDERATIONS

#### Introduction

Monitoring trace metals in the atmosphere is important because of the toxic effects resulting from continuous exposure to high concentrations of certain metals. Increasing world-wide industrial activity has resulted in an almost unrestricted growth of the air pollution problem. The situation has been further aggravated by the energy crisis because it causes the use of cheap, low-grade fuels. For these reasons, the amounts of trace metals in the environment have increased dramatically during this century.

In order to understand the impact that trace metals have on general health, techniques are needed to assess their concentrations in air. Until very recently, measurement was possible only on 24-hour average samples because of the insensitivity of most commonly available analytical methods. These 24-hour samples give only an incomplete picture of the magnitude of the problem because they preclude daily cyclical information. With the availability of the extremely sensitive analytical technique, square-wave anodic stripping, it was thought that the much needed time variations in the concentrations of airborne copper, lead, cadmium, and zinc could be measured accurately and precisely.

In the process of developing a method suitable for such low-level

analysis, problems related to the optimal sampling procedure and sample treatment were encountered. These matters are discussed in Chapters 2 and 3. Purposefully, the discussions in these chapters includes parameters related to the measurement, not only of the main elements (i.e. copper, lead, cadmium, and zinc), but also many other trace metals. It is hoped that this background information will benefit other studies. The remaining chapters present the theory of square-wave polarography and discuss the method for the determination of the time variations in the airborne concentrations of copper, lead, cadmium, and zinc.

The following sections consider some aspects related to the abundance, uses, and potential problems of the metals studied.

### Copper

Copper is a reddish, lustrous, ductile, and maleable metal that becomes dull when exposed to dry air and gradually coated with the green basic carbonate when exposed to moist air. Its content in the earth's crust is nearly 0.01 percent. The yearly world production is more than six-million lbs. and it is used for the manufacture of brass, bronzes and other alloys, and electrical conductors, ammunition, and works of art.

Copper is present in all living matter, both plant and animal. In plants, it may be associated with the formation of chlorophyll. In animals, its association with hemoglobin has been stressed. It also forms part of important biological complexes such as hemocyanin (an analog of hemoglobin), pheophytin (an analog of chlorophyll), and of

certain oxidizing enzymes, such as ascorbic acid oxidase, polyphenol-oxidase, laccase, and tyrosinase. Thus, it can be seen that copper is an essential trace element and consequently its air-pollution problem is difficult to evaluate. Copper itself probably has little or no toxicity, although there are conflicting reports in the literature. Soluble salts, notably copper sulfate, are strong irritants to the skin and the mucous membranes. Copper oxide fumes can cause metal fume fever [1]. However, these effects are related to the high concentrations possible in industrial exposure and not to the low levels expected in air. On the other hand, study of the time variations of the ambient concentrations of this metal, along with others, can prove valuable in the "fingerprinting" of a pollution source via its metal emissions.

#### Lead

Lead is a bluish-white, silvery, grey metal, very soft and malleable, easily melted, cast, rolled, and extruded. The extent of its occurrence in the earth's crust is about 15 g/ton, or 0.002 percent, chiefly as lead sulfide in galena.

The hazard of lead as a powerful poison has been recognized since early civilization. Water pipes and primitive tools were made of lead; vessels used for cooking, eating, and wine storage contained the metal.

Lead is produced in larger quantities than any other poisonous heavy metal. The current world production is estimated to be seven million pounds, 6.2 of which are produced in the northern hemisphere [2].

In modern times, lead has played a predominant role in the occupational diseases among miners, smelters, automobile finishers, foundry workers, storage battery workers, typesetters, sheet metal workers, and spray painters. Paint containing lead, specially white lead, chrome green, and chrome yellow, as well as lead in the solder used to seal food cans, have contributed materially to the incidence of plumbism (chronic lead poisoning).

During the past four decades, the development of the lead alkyls (namely, tetraethyl and tetramethyl lead as antiknock additives for gasoline) has created one of the most hazardous sources of environmental pollution. One gallon of common gasoline contains up to 4 g of lead [3]. About 300,000 tons of lead were used in gasoline additives in 1968. This amount constitutes nearly 25 percent of the total lead used in the United States [4]. Over 180,000 tons of lead are estimated to be emitted annually into the atmosphere by automobiles, trucks, and buses [5]. In a large city like Cincinnati, this emission gives lead levels of about  $1.6 \mu\text{g}/\text{m}^3$ . During peak traffic periods the levels can be increased vastly. For example, in Los Angeles as much as  $71 \mu\text{g}/\text{m}^3$  have been recorded [6].

Airborne lead can be absorbed easily because of the small size of the particles (down to less than  $1 \mu\text{m}$ ). These particles are readily inhaled into the alveoli [7]. There the lead is absorbed by the blood and then accumulates in the bones where it replaces calcium. High levels affect the formation of blood in two important ways: 1) it produces stippling of red blood cells and anemia by retarding the normal maturation of red blood cells in the bone marrow, 2) it inhibits the

synthesis of hemoglobin by interfering with two substances, delta-amino levulinic acid and coproporphyrin III, necessary for the formation of hemoglobin.

Advanced poisoning with lead may cause brain damage, blindness, and death. For these reasons it is important to be able to monitor short-term variations in the airborne concentration of this metal. Peak concentrations, and not daily average ones, are the data that will be more relevant to an epidemiological appraisal of lead.

#### Cadmium

Cadmium, a silver-white metal, is soft, ductile, and highly resistant to corrosion. It is mined in conjunction with other metals, mainly zinc, and recovered from flue dust of copper and lead smelting plants and as a side product in the electrolytic recovery of zinc. In the mid-1920's it was used pharmaceutically in the treatment of syphilis and malaria [8]. However, once its toxic properties were recognized, this therapy was abandoned. Nowadays, of the 12.6 million pounds consumed in the United States [9] approximately 50 percent is used for electroplating and another 20 percent as a constituent of stabilizers for polyvinyl chloride. Most other uses are in conjunction with alloys, particularly with gold in jewelry. In soldering, cadmium is combined with copper, lead, tin, zinc, and silver.

Nickel-cadmium batteries are used in military aircraft, guided missiles, and in refrigeration of railway cars. Cadmium-copper alloys are used in the overhead wires for street and railroad cars. The automobile and aircraft industries use cadmium in engine parts. It is



also used in radio and television manufacturing.

The yearly cadmium emission into the air is estimated to be more than half a million pounds [10]. Much of the metal is emitted into the atmosphere during the manufacture of fertilizers and pesticides. Incineration and melting down of cadmium-containing products, specially scrap steel, automobile radiators, plastic bottles, auto seats, furniture, floor coverings, and rubber tires, constitute 52 percent of the total estimated annual emission [9]. In addition, cadmium is inhaled by the smoking of cigarettes, one pack of which contains approximately 30  $\mu\text{g}$  of cadmium; 70 percent of this amount escapes into the air with smoke [11].

Cadmium has no known biologic function. It is toxic to almost all systems and functions of human and animal organisms [12]. It is absorbed into the human organism without regard to the amount already stored, nor does there appear to be a mechanism to maintain a constant level in blood and other body fluids [13]. Cadmium inhibits the function of the enzymes containing the sulphhydryle (SH) groups, which are dependent on the presence of zinc, cobalt, and other metals. There is evidence that cadmium acts on the smooth muscle of the blood vessels, either directly or indirectly through the kidneys [13]. It has also been linked to arterial hypertension in animals [14] and in humans [15] and found to have mutagenic and carcinogenic effects in animals [16].

Because of the expansion of the cadmium industry and our increasing awareness of the health hazard of cadmium, the analysis of the airborne concentrations of this metal plays an important role in the study of air pollution.

### Zinc

Zinc is a bluish-white, lustrous metal which has been known since very early times. Naturally it occurs as 0.02 percent of the earth's crust in the form of zinc blende ( $\text{ZnS}$ ), associated with lead and iron sulfides [17]. It has found extensive application in industry where it is used for galvanizing sheet iron, as an ingredient of alloys such as bronze, brass, German silver, and special alloys for die-casting. It is used as a protective coating for other metals to prevent corrosion, for extracting gold by the cyanide process, and for many other uses.

The annual emission of zinc from stationary combustion sources is estimated at 4.6 million pounds [10]. Nevertheless its role as a pollutant is difficult to assess because zinc is commonly associated with other contaminants, especially cadmium and lead. It is emitted, mainly as zinc oxide, from factories that produce copper, lead, and steel, and from secondary processing operations that recover zinc from the incineration of zinc-bearing materials.

Zinc is an important trace element, necessary for the proper function of many enzymes. It plays a part in the normal development of the skin and the skeleton [18]. It also controls the normal synthesis of proteins and of deoxyribonucleic acid (DNA), the principal constituent of the genes. An adult man stores between 1.2 and 3 g. The average daily intake is 10 to 15 mg, but normal blood levels are remarkably constant, namely 0.8 to 1.6 ppm.

To humans, zinc is usually considered nontoxic in open atmospheres, but inside factories, inhalation of zinc or zinc compounds

at a level of 48 to 74 mg/m<sup>3</sup> for 10.5 and 12 minutes, respectively, has caused the occurrence of metal fume fever [19]. These concentrations, however, are extremely high and, hence, not applicable to air pollution problems where urban concentration estimates are in the range of 0 to 1 µg/m<sup>3</sup> [20]. Zinc, like copper, is an important metal to be monitored in the atmosphere because variations in its concentration, along with relevant meteorological data, can provide a way to find a pollution source. This "fingerprinting" of pollution sources through their daily emissions can only be implemented if adequate techniques are available. The techniques not only require analytical methods of adequate sensitivity, as e.g. square-wave polarography, but must also include appropriate ways of sampling, treatment of sample, and data processing. To study the complex in its full extent is the purpose of this work.

## CHAPTER II

### SAMPLING OF PARTICULATE MATTER

#### Introduction

Most air pollution problems require sampling and analysis of the contaminated atmosphere. From the standpoint of air pollution, the purpose of collecting samples is generally to determine the type and properties of impurities, and the degree of contamination. Sampling and analysis also provide quantitative information useful in the development of remedial measures, as evidence for legal purposes, as basis for police or control action, as standards for equipment performance, and as future reference.

An improperly obtained sample makes the subsequent analysis practically worthless because no analysis can be better than the sample. Very likely there are as many incorrect results due to improper sampling as from combined errors of manipulation, measurement and calculation. It should be apparent, therefore, that the importance of proper and adequate sampling cannot be overemphasized.

The purpose of this section is to describe some general guidelines to be followed in collecting samples for the purpose of studying air pollution problems as well as to describe the principles of the common sampling techniques and devices.

#### The Representative Sample

Obtaining a representative sample of a contaminated atmosphere

presents some very special and difficult problems. It is difficult to sample air containing suspended particulate material without altering the concentration of particulate material in the sample. In addition, due to the extremely small concentration of pollutants and to the many factors that influence their concentration in the atmosphere, careful planning when attempting to sample is advisable in order to avoid being confronted with the crude fact of sampling at the "wrong time". Samples should be collected with knowledge of how results are to be used and of the accuracy required. These requirements are subject to many variations. All too frequently, samples are collected that, will not and cannot provide the information that is necessary, regardless of the analytical techniques applied.

It is obvious to any analytical chemist that proper sampling is a most important part of the total process of air analysis. Unfortunately, the analytical chemist seldom has the opportunity or time to collect the samples and he can only give guidance to those that do. It is necessary, therefore, that he consider exactly what he wants to sample and how parameters such as sampling rate and frequency will affect the end result. The size of the sample will also be of importance, although in most cases the detection limits of the intended method of analysis will dictate this. A brief discussion of these factors is given below.

#### Sampling Rates

In general, samples for particulates should be collected under isokinetic conditions, that is at the same rate of flow as the flow of

the contaminated air stream. Strictly speaking, isokinetic sampling occurs only when the suspension enters the orifice of the sampling device without disturbance or acceleration of any kind. There must be no eddy formation near the orifice and no change of direction as the suspension enters the orifice. The air carrying the particles must be flowing uniformly. Most authorities agree, however, that isokinetic sampling is not necessary for aerosol particles smaller than five to ten micrometers mean diameter. Because of the small settling velocities of particles below the size of this range, their own motion does not vary significantly from the motion of the air in which they are borne.

Recent studies indicate that at least 75 percent of the Zn, Cu, Cd, and Pb occurs in particules smaller than 2  $\mu\text{m}$  [21,22]. This finding supports the idea that isokinetic sampling may be unnecessary to obtain an adequate sample of these metal aerosols. For more information on the topic of isokinetic sampling the reader is referred to Watson [23], who has derived a tentative semiempirical formula to determine the magnitude of errors due to anisokinetic sampling.

#### Estimation of Sample Size

In order to perform a satisfactory analysis, it is necessary to have a sample that contains amounts of contaminants in sufficient quantities to permit proper identification and measurement. The collection of an obvious excess of sample may seem to be an adequate solution; however, this procedure is generally inefficient in other aspects, as it prevents obtaining the maximum frequency of sampling. By careful adjustment of the sample size downward, from excessive proportion, to a size based upon specific needs, we may be able to sample more

frequently, thereby acquiring more complete information of the contaminated atmosphere.

Several factors must be considered before the size of the sample can be estimated. One of these is the expected concentration of the contaminant in the air. A possible source which may permit a reasonable estimate of the expected concentration is the data from the National Air Sampling Network. The Network consists of a group of preselected sites, mainly in the United States and its territories, where one or more units of air sampling equipment is set up. These units are operated by volunteers representing some local agency. The samples thus obtained are forwarded to the Environmental Protection Agency (EPA) in Research Triangle Park, North Carolina for physical and chemical analysis. The results of the analysis are returned to the agency operating the equipment, and are also used by EPA for compliance, statistical analysis, and as bases for publications showing nation-wide trends and correlations. An example of such data is given in Table 1. It shows the national distribution of the concentration of metals in urban areas [20]. This average metal concentration is useful as a first approximation to estimate what to expect in a particular area. But even more pertinent information can be obtained from data compiled by the EPA for specific cities. Table 2, for instance, shows the urban cumulative frequency distribution of twelve metals for the Atlanta metropolitan area for the year of 1968 [24].

Alternatively, if emission estimates or data from source

Table 1. National Distribution of Concentrations of Metals  
in Urban Quarterly Composite Samples [20].  
( $\mu\text{g}/\text{m}^3$ )

Metal	Year	ND <sup>a</sup>	Number of samples in concentration range <sup>b</sup>													
			$\times 10^{-4}$			$\times 10^{-3}$			$\times 10^{-2}$			$\times 10^{-1}$			$\times 1$	
			1-2	2-5	5-10	1-2	2-5	5-10	1-2	2-5	5-10	1-2	2-5	5-10	1-2	5-10
Antimony	1966	398							2							
	1967	451							1							
Beryllium	1966	349	22	24	4	1										
	1967	375	27	39	9	2										
Bismuth	1966	338			29	21	7	1	3	0	0	0	1			
	1967	416			14	11	9	2								
Cadmium	1966	304						50	27	15	2	2				
	1967	316						67	35	24	6	4				
Chromium	1966	274						61	35	25	3	2				
	1967	321						60	38	29	3	1				
Cobalt	1966	396						4								
	1967	447						3	1	0	0	1				
Copper	1966	8						22	87	138	101	32	10	1	1	
	1967	11						16	63	130	125	76	28	3		
Iron	1966	12										9	78	115	114	67
	1967	15										18	85	103	122	99
Lead	1966	5									4	11	78	166	102	31
	1967	6									2	7	57	178	147	53
Manganese	1966	24						38	70	129	80	39	17	3		
	1967	23						29	64	157	101	48	20	9	1	
Molybdenum	1966	311				19	35	21	7	3	4					
	1967	342				22	57	21	3	3	4					
Nickel	1966	120						63	110	77	26	4				
	1967	134						81	116	90	20	9	2			
Tin	1966	189			31	18	76	54	28	2	2					
	1967	200			53	29	76	56	33	4	1					
Titanium	1966	216						55	51	49	22	7				
	1967	215						43	70	70	38	15	1			
Vanadium	1966	195				10	31	43	44	29	22	24	2			
	1967	144				58	41	50	57	46	19	26	8	3		
Zinc	1966	236								13	26	47	50	23	5	
	1967	271								25	25	51	53	26	1	

<sup>a</sup>Not detectable; below minimum detectable level. First entry is in range of minimum detectable level.

<sup>b</sup>If a number lies on the class bound, it falls in the next higher interval.  
For example, 0.0002 falls in the 2 to 5 range.



Table 2. Air Quality Data for Metals in Atlanta Metropolitan Area for 1968. [24]  
Urban cumulative frequency distribution in  $\mu\text{g}/\text{m}^3$ . Total of 26 samples.

Metal	min.	Frequency Distribution, %									max.	mean
		10	20	30	40	50	60	70	80	90		
Be	0.0	no. of samples (26) below minimum detection limits exceeds 50%									0.0	
Cd	0.0	no. of samples (15) below minimum detection limits exceeds 50%									0.018	
Cr	0.0	0.0	0.0	.009	.010	.011	.013	.021	.038	.062	0.081	0.021
Co	0.0	no. of samples (21) below minimum detection limits exceeds 50%									0.009	
Cu	0.0	no. of samples (14) below minimum detection limits exceeds 50%									0.110	
Fe	0.2	0.8	1.0	1.2	1.7	1.8	2.3	2.8	3.0	3.7	6.9	2.3
Pb	0.3	.54	.59	.60	.69	.97	1.4	1.6	1.9	2.2	3.5	1.21
Mn	0.0	0.0	0.0	0.0	0.0	.02	.04	.05	.06	.13	0.78	
Ni	0.0	no. of samples (18) below minimum detection limit exceeds 50%									0.0023	
Sn	0.0	no. of samples (23) below minimum detection limit exceeds 50%									0.020	
Ti	0.0	0.0	0.0	0.0	.10	.11	.13	.15	.18	.24	0.34	
V	0.0	no. of samples (26) below minimum detection limit exceeds 50%									0.0	

sampling are available for a particulate source or for a small number of sources, these may well assist in estimating the concentration downwind by the use of diffusion equations. In the more complex problem of estimating the concentration of a particular pollutant in the air over a metropolitan area, approximations more complex in nature are employed [25]. Valuable source inventory data has been published [10] which permit the formulation of estimates of pollutant concentration, including trace metals, provided that the number and variety of contributing sources are known or can be satisfactorily approximated.

Another factor which needs to be considered in estimating the sample size is the efficiency of the sampling procedure. The removal of particulate from a volume of air is often assumed to be 100 percent, i.e., that a filter collects all of the particles from the air passing through it. Such assumptions are not necessarily correct. It is well to note that the efficiency of devices which collect particulate matter can only be properly states in terms of a defined range of particle size.

For sampling metal aerosols, therefore, a device capable of greater than 90 percent retention efficiency for particles between 0.1 and 10  $\mu\text{m}$  would be best. This size range includes both the bulk of the particulate mass and a large fraction of the number of particles.

Finally, the requirements of the analytical procedure must also be considered. The minimum practical amount which can be identified and measured with confidence is largely determined by the method of analysis employed. Since the instrumentation available to different

laboratories will vary, it is important to examine within our own capabilities and resources what minimum amount of pollutant will be needed. In the determination of trace metals in environmental samples a great variety of modern instruments are used for the final analysis. A general discussion of this will be presented in the chapter on analysis of air samples.

In summary the relationship between the three broad factors that enable to estimate the sample size in terms of air volume can be illustrated by the following equation:

$$\text{sample size} = \frac{\text{Requirement of Analytical procedure (weight)}}{\text{(volume) Expected concentration (wt/vol) of contaminant}} \times \frac{1}{\text{Efficiency of sampling procedure}} \quad (1)$$

#### Sampling Frequency

In the design of an efficient sampling program, one of the most difficult tasks is the determination of when and how often samples should be taken to determine the concentration of air pollutants in an area. One of the initial steps toward solving this problem is to consider the patterns of specific factors affecting the concentration of the specific contaminant we want to sample. For instance, a study of the available meteorological data of the general area to be sampled should prove useful. Parameters such as precipitation, temperature, wind speed and direction, and temperature inversions should give an idea as to when to expect a higher pollutant concentration and the

best location to place the sampling equipment. In addition, a study of the type of pollution sources in the area and patterns of their activities will help determine the best times for sampling.

Ideally, one should take an air sample as frequently as it is possible. This assures that a complete picture of the pollution extent and situation can be constructed. But even more important is the fact that shorter-term variation in the concentration of pollutants can be monitored. These changes would otherwise escape attention. In the field of airborne metal trace analysis, sampling frequency has been limited to sampling every 24 hours because of the lack of sensitivity of the available instrumental analysis techniques. The amount of sample required for an adequate analysis was in the order of several hundred milligrams which could only be furnished by sampling nearly 3000 cubic meters of air. With the advent of modern instrumentation methods, such as square-wave polarography, flame-less atomic absorption and others, a higher sampling frequency has become a reality.

### Sampling for Particulates by Filtration

#### Introduction

The trace metals forming part of the atmospheric aerosol may be trapped by a variety of methods, each of which is based on different principles. Filtration, sedimentation, impactation, and precipitation are most commonly used. Each offers distinct advantages depending on the intended purpose of the sample. Filtration is by far the most popular method because of its low cost and simplicity. In contrast to other methods, it possesses the capability of handling high flowrates.

The great variability in the available size of filters has proved to be another advantage of filtration. By varying the size of the paper the volume of the air sampled can be varied while still maintaining the same linear flowrate through the filter. Filter holders are designed for a large range of sizes and, therefore, meet a variety of problems.

Furthermore, appropriate filters can be obtained that are capable of sampling over a wide range of conditions of temperature, humidity and dust loading, and adapt to a variety of analysis schemes ranging from microscopic examination to elaborate chemical separation and digestion processes. For these reasons, most procedures dealing with the determination of airborne trace metals have depended on filtration as their sampling step.

The fact that filtration inherently possesses numerous advantages for air pollution sampling does not mean that this method lacks disadvantages that can be of significance and are not encountered in other methods. One of these difficulties is related to the inhomogeneity of filter paper. In comparison, for an impactation device, when the operating characteristics are set, they remain relatively constant. In filter sampling, however, the filter paper is changed between each sample collection, or a different portion of it is used, as in the case of sampling with a filter tape, thus, operating characteristics may vary. Filters may be obtained with a minimum of variability from filter to filter, however, not very readily. In the determination of trace metals this factor presents a serious problem, specially when the variability is in terms of the metal impurity

level in the filter. It is difficult to obtain reproducible results in this case unless so large a sample is taken that the variations in the filter are no longer significant when compared to the magnitude of the metal in the sample. This approach, although necessary at times, prevents a maximum sampling frequency as was discussed previously. The differences between lots of filters may also be so large, that re-evaluation of filter blanks becomes necessary, or even a quality control scheme has to be implemented.

Another case in which filters are at a disadvantage is in conjunction with selective particle sizing. A cascade impactor can, theoretically, be designed so that particles of different size ranges can be collected on different stages of the impactor. Such size separation can hardly be done with filters, although some rough gradations are possible.

#### Filtration Theory

There are several mechanisms that play an important role in the collection of particulate matter in air. The one most widely known is direct interception which can be considered analogous to mechanical straining. The interception takes place when a particle following the air movement streamline comes within a distance from the filter media which is equal to, or less than, the particle radius and therefore, the particle comes into contact with the filter medium. As with simple straining, this mechanism predominates where the particles are greater in diameter than the interfiber distance, or pore size.

The direct interception mechanism is by no means the primary mechanism of filtration. Other mechanisms such as diffusion, inertia, and electrical forces also play a very important part in the retention of particles and thus contribute to the overall efficiency of filtration. The collection of particulates on a filter medium by diffusion will depend on the particle concentration gradient between the filter fiber and the air passing between fibers. The highly particle-concentrated air stream diffuses to the filter fiber where the particle concentration is nearly zero. The effectiveness of the diffusion mechanism (limited to particles below  $1\text{ }\mu\text{m}$  in diameter) is specially significant for particles below  $0.1\text{ }\mu\text{m}$  in diameter. These are the particles which are subject to large random (Brownian) motion caused by collisions with individual molecules. The contribution of diffusion will also depend on the amount of time the particle is allowed to transit through the filter media which will in turn be dictated by the linear rate of flow, the filter thickness, and the interfiber distance.

When the airborne particle is above  $1\text{ }\mu\text{m}$ , inertial collection is of greater importance. Due to their mass and velocity these particles will possess enough momentum to continue largely undeviated from their previous paths even when the air stream turns. If the inertia of the particle causes it to strike a filter fiber during the passage of the air stream around the fiber, the particle will be collected. This mechanism will play a major part with high linear velocities of air flow.

Although the magnitude of the effect of electrical forces on

particulate collection is not known, experiments performed by Gillespie [26] indicate that both atmospheric particles and filter media possess electrical charges and that attraction between them, if oppositely charged does cause collection to be accomplished. For this reason, many investigators feel that such a mechanism has a part to play in the filter sampling of air, specially in the collection of particles smaller than the pore size.

Finally, it is important to consider that during an actual filter sampling process, these mechanisms will be working simultaneously. Hence, the combined collection factors may result in a better than expected collection efficiency. Of course, other mechanisms such as reentrainment of particles into the airstream and particle bounce-off will complicate the situation, preventing the retention of all particles which come into contact with the filter material.

#### Collection Efficiency of Filters

In filter sampling, all of the collection mechanisms take place simultaneously and their effects are algebraically additive. Therefore, the overall collection efficiency of a filter will depend on the extent to which each mechanism is significant in the filtering process. The role of diffusion, inertia, electrical forces, and direct interception will in turn be dependent on parameters such as filter material and interfiber distance, sampling flowrate, particle-size distribution of the aerosol and others, as previously discussed.

The terms in which the collection efficiency of filter sampling is reported in the literature varies. The most common is to determine



the percent penetration (percent passing through the filter) of a certain particle size as a function of the linear velocity (volume rate of flow divided by the filter area) through the filter, or as a function of the particle size. Table 3 presents an example of the penetration tests on some filters as reported by Chambers [27].

Another way of presenting the efficiency is to report the percent collected of a certain particle size, as a function of linear velocity through the filter. An example from data reported by Fitzgerald and Detwiler [28] is presented in Table 4.

Finally, some workers prefer to report the efficiency as a mass-collection efficiency based entirely on the percentage of the mass of the airborne particles collected. Although efficiencies of these types are useful, it would be most difficult to use them to determine the fraction of the atmospheric particulate collected unless the particle size distribution existing in the atmosphere is known, and percent penetration tests have been performed using this size distribution. Even then, the results could be used only with caution. A number of different types of particulates have been used in these efficiency tests, including di-octyl phthalate (DOP, Table 3) smoke, atmospheric dust, duraluminium dust, polystyrene aerosols, and lead fumes. The experimental results of the various investigators often appear to be in great disagreement for many filter media. A case in point is the efficiency of Whatman 41 for submicron particles as presented in Table 3. Fitzgerald [28] found that the percent penetration of  $0.18 \mu\text{m}$  duraluminium particles was 14.8 percent at a linear velocity

Table 3. Filtration Efficiencies of Some Types of Chemical Filters [27].

Filter Type	Percent DOP* Penetration at 28 feet per minute
Whatman 1	27
4	73
32	0.35
40	8
41	75
42	.22
44	.5
50	.9

\*DOP is di-octyl phthalate, particles 0.3 micrometers in diameter.

Table 4. Collection Efficiency of Various Filter Media of Duraluminum Particles at Specified Face Velocities. [28]

Paper Designation	Face Velocity ft/min	Collection Efficiency* Spread in Percent
Whatman 40	80	98.2 - 99.6
Whatman 41	200	97.6 - 98.0
Atomic Energy Commission 1	40	99.5 - 99.9
MSA Glass Fiber 1106-B	200	99.2 - 99.8

\*Efficiency range for particles 0.18 to 2.1 micrometers.

through the filter of 4 ft/min and it decreased to 1.6 percent when the velocity was increased to 100 ft/min. Chambers (Table 3) performed his tests at a linear velocities of 28 ft/min and 20 ft/min with 0.3  $\mu\text{m}$  DOP particles. Based on Fitzgerald's result one would have predicted that the percent penetration of the DOP particles should be greater than 1.6 percent but certainly smaller than 14.8 percent because of the linear velocities Chamber used. Instead Chamber found percent penetrations of around 75 percent as can be seen in Table 3. This discrepancy may be explained by a subsequent study by Fitzgerald and Detwiler [29] in which they found that collection efficiencies depend not only on particle size and linear velocity through the filter, but also on the type of aerosol. They found, for example, that Whatman 40 and 41 were more efficient for collecting solid duraluminium particles than for  $\text{KMnO}_4$  particles in the size range of .005 to .1  $\mu\text{m}$ . This may explain some of the difficulties encountered when trying to compare studies of the filtration efficiency and points toward caution when attempting to extrapolate the results to the collection of atmospheric particulate. As Neustadter [30] pointed out recently, it should be noted that the DOP and other similar procedures are severe tests designed to rate absolute filters under laboratory conditions over a very limited time intervals. As such, they do not directly apply to the evaluation of a filter collecting a large range of particle sizes, in relatively polluted atmospheres containing a wide variety of chemically diverse substances, over larger time spans.

One additional factor should be mentioned in relation to filter efficiency. During the time that the filtration is in operation, the

increasing amount of particulates that accumulate on the filter will cause the collection efficiency to improve, as sampling continues. This seems to be a case in a study by Dams [31] which compared Whatman 41 with very efficient (99 percent retention) polystyrene filters in an actual 24-hour field test. Here, the conclusion was that little or no difference could be seen in collection efficiency. Presumably, this is a consequence of the rapid plugging of the W41 air passages by the particles being collected; a phenomenon verified by Lidiken [32] for  $0.365 \mu\text{m}$  aerosol collected at a flow rate of  $0.28 \text{ m}^3 \text{ min}^{-1}$  and at a concentration of  $500 \mu\text{g m}^{-3}$ , which showed collection efficiency rising from an initial value of 75 percent to over 95 percent in less than 30 minutes.

Although this rise in the efficiency is favorable, it is accompanied by an increased resistance in the filter to airflow which decreases the flowrate and thus perhaps interferes with the sampling procedure. As a consequence, greater uncertainty in the calculation of the sampled air volume will result.

#### Characteristics of Filter Media

There is a wide variety of filters which may be suitable for sampling airborne trace metals. These filter media may be broadly divided into four categories: cellulose fiber, glass fiber, mixed fiber and membrane filters. In this section, each category will be discussed in terms of their general characteristics, and of the sampling and analysis considerations.

Cellulose Fiber Filters. These filters are manufactured from high purity cotton cellulose and although not designed specifically for

air sampling, a number of them possess the purity, consistency, uniformity, and reliability of performance necessary for air pollution work.

(1) Sampling considerations. The cellulose fiber filters have seen extensive application in the area of air sampling because they are relatively inexpensive, available in a large range of sizes, and show excellent tensile strength and resistance to wear. Most commonly they are used with low volume sampling devices because the pressure drop is often high and increases linearly with flowrate. Yet some workers have reported a marked increase in the efficiency for the collection of very small particles (less than  $1\text{ }\mu\text{m}$ ) when flowrates in the neighborhood of 200 linear feet per minute were employed [30]. No significant difference in the retention efficiency of a cellulose filter, Whatman 41, and fiber glass or polystyrene filters has been reported when sampling with a high volume sampler for 24 hours [31].

The ability of cellulose filters to withstand gas flow, pressure, and other mechanical stress enables cellulose filters to be used with a variety of sampling devices for short-term automatic sampling. Rolls of Whatman 4 have been used routinely in conjunction with tape samplers to examine time variations in the concentration of particulate matter as well as that of selected gaseous pollutants.

Of course, because of their composition, cellulose filters can only be used effectively at maximum temperatures in the range of 80 to  $150^{\circ}\text{C}$ , depending on the particular filter under consideration. This fact prevents their use for high temperature sampling such as the one encountered in stack sampling.

(2) Analytical Considerations. The low ash content of cellulose filter makes them highly suitable for analytical preparation where dry or chemical ashing as required. In general, cellulose fiber filters allow considerable dust to be buried in the fibers and thus require an involved sample treatment. However, some of these filters, such as Whatman 54 and 541 have acid hardened surfaces which allow the collected particles to be removed simply by washing. A definite advantage is that some cellulose filters can be found with very low levels of metallic contamination because of acid pretreatment from the manufacturer. In Table 5, a list of some of the impurities commonly found in cellulose filters is presented.

Glass Fiber Filters. These filters are unique among the wide range of fibrous materials used commercially as filtration media. The glass microfibers differ from naturally occurring cellulose fibers in that they are circular in cross section, are of controlled diameter, and are made extremely fine. They also have a considerably higher density than cellulose and most other man-made fibers. For reasons that will be examined below, these filters enjoy increased popularity as an air sampling media.

(1) Sampling Considerations. There is no conflicting evidence in the literature in relation to the extremely high collection efficiency of glass fiber filters. It is generally accepted that these filters will trap 0.3  $\mu$ m DOP aerosol with an efficiency higher than 98 percent under a variety of flowrates. This characteristic, along with the ability to tolerate a wide temperature range and maintain a

Table 5. Whatman Filter Papers Typical Impurities,  
ppm [33].

Element	Qualitative	Ashless	Hardened Ashless
Aluminum	3	3	1.5
Antimony	-	0.03	0.01
Arsenic	<0.2	<0.2	<0.2
Barium	-	<1.0	-
Boron	0.5	0.3	0.2
Bromine	-	0.22	0.22
Calcium	127	13	7
Chlorine	57	22	20
Chromium	-	0.3	0.04
Copper	1	0.7	0.4
Fluorine	<0.5	<0.5	4
Iron	9	5.5	1.1
Lead	0.2	<0.1	<0.1
Magnesium	7	2	1
Manganese	<0.1	0.06	0.03
Mercury	0.1	0.05	0.05
Nitrogen	16	<10	107
Potassium	5	0.5	0.5
Silicon	36	17	16
Sodium	86	20	7
Sulphur	<10	<10	<10
Zinc	2	0.6	0.4



relatively constant flowrate under different loading conditions, make this filter ideal for sampling particulate matter.

Because of the non-hygroscopic nature of the glass fibers, these media will maintain a constant weight under wide variations of ambient humidity, thus allowing them to be used in areas where humidity is high. Their glass media also makes them the filter of choice for most corrosive atmospheres. All of the filters in this category are quite friable and must be handled with care.

(2) Analytical considerations. While glass-fiber filters show excellent characteristics for particulate matter sampling, the opposite is true when it comes to the analysis of trace metals. Glass-fiber filters cannot be ashed, therefore some other type of chemical preparation must be used. Furthermore, the common practice of dry ashing at high temperatures, as a method of oxidizing organic matter on glass filters prior to acid dissolution of the residues, should be greatly discouraged. Several authors have reported losses of the low temperature melting metals including Pb, Cd, Cu, and Zn [33,103]. Although it was thought at first that the explanation for these losses was the volatilization of metals at high temperatures, Kometani [35] has discovered that the cause is directly related to the glass fiber media. He has shown that metals such as Pb, Zn, Cu, and Cd react to varying extents with the glass at high temperature to form insoluble metal silicates. This prevents the total metal recovery later.

Another problem in the analysis of trace metals collected on fiber-glass filters arises from their high impurities levels [36].

For this reason it is not possible to obtain short term variations of the concentration of metals. One has to sample for a long period of time before the sample metallic concentrations are safely above the background filter blank levels. Some of the common contaminants in these filters are Al, Na, Fe, and Zn, but the levels of Cu, V, Pb, and Ti are also significant as can be appreciated from Table 6.

Mixed Fiber Filters. This type of filter is manufactured by the interweaving of fibers of different natures with the purpose of adding reinforcement, durability, improving the efficiency, and extending the range of applications of a filter media. For this reason, each particular kind of mixed-fiber filter has to be examined independently and according to its composition in order to determine its characteristics. The advantages and disadvantages that this category of filter will have in the sampling and analysis of particulate matter will also be directly related to the individual fiber constituents.

Membrane Filters. This filter medium consists of dry gels of cellulose esters, usually produced as cellulose acetate, or cellulose nitrate. The filters are cast on a smooth, flat substrate and exposed to a controlled atmosphere. The process can regulate both the internal membrane structure and the pore size.

(1) Sampling considerations. Membrane filters are typically very brittle and require careful handling. In air sampling they should be backed by some support structure to avoid breakage. The filters are not too well suited to stack sampling, as they have an operating temperature range comparable to cellulose fiber filters.

Table 6. Impurities in Glass Fiber Filters (ppm) [37,31].

Element	Concentration	Element	Concentration
Cl	< 100	Cr	16
Mn	3	Fe	800
Na	5800	Pb	160
Al	1800	Ni	< 16
Br	< 100	Si	$1.4 \times 10^6$
Cu	< 50	Ti	160
V	140	Zn	$3 \times 10^4$
Be	8		

One factor of interest is that the particle collected by membrane filters has size consistently smaller than the interfiber distance. A possible explanation for this increased efficiency is the role of electrostatic forces in the collection process at the membrane filters.

Finally, a factor that should be considered when planning to sample with these types of filters is the limited air volume that can be sampled. This restriction results from the appreciable pressure drop cellulose ester filters suffer as they load with particulate matter. In addition, it is not recommended to sample more air than will result in a single layer of particulate. When a second layer builds up, it has a tendency to slough-off, causing the loss of part of the sample.

(2) Analytical considerations. Like cellulose filters, membrane filters have the advantage of being readily ashed, leaving very little residue. This can be a definite advantage in some analysis schemes. A number of chemicals dissolve or otherwise affect these filters; this may also aid to establish an analysis procedure.

From the standpoint of metallic impurity levels, cellulose ester filters are much cleaner than fiber glass but more contaminated than cellulose fiber filters. The factor of the filter impurity levels becomes more important and indeed may become the limiting factor in determining the detection limits of a technique when the sample duration is one to two hours or less. The filter impurity levels of some membrane filters is presented in Table 7.

Summary of Filter Media. No single type of filter can be said to be fully appropriate for all types of air sampling. In selecting

Table 7. Filter Impurity Levels in Millipore Filters [31].

Element	Paper Filter Designation			
	HAWPO25	HAWPO47	AAWPO25	AAWPO47
Cl	1,000	1,000	1,700	1,000
Br	4	3	<5	<2
S	-	-	4,800	-
Na	600	330	520	400
K	130	100	120	100
Mg	<300	<200	400	200
Ca	670	250	500	370
Ba	<100	<100	<100	<100
Al	20	10	15	10
Sc	<0.05	<0.01	<0.01	<0.05
Ce	<0.5	<1	<0.5	<0.3
La	<0.1	<0.2	<0.5	<0.2
Ti	15	5	10	<10
Fe	40	<300	80	40
Mn	7	2	2.5	2
Co	0.2	<1	0.4	0.1
Ni	<8	<50	14	<20
Ag	<4	-	<3	<1
Cu	20	40	85	60
Zn	25	20	10	7
Sb	0.5	3	0.4	1
Cr	15	14	20	15
Hg	<0.4	<1	<1	0.5
V	<0.06	0.09	<0.2	<0.05

the best one for a specific purpose, many factors should be considered including the general filter characteristics, collection efficiency, sampling conditions, flow resistance and type of subsequent analysis. Nevertheless, when attempting to sample air for trace metal analysis there is one factor that should weight heavily: the impurity levels of metals in the filter. As was mentioned before, high metal levels restrict the detection limit of the analysis method and prevent sampling as frequently as it would otherwise be possible. The data presented here seems to indicate that a cellulose filter such as Whatman 41 is most suitable for monitoring time variations in airborne trace metals because it possesses the tensile strength and wear resistance necessary for air sampling, combined with the high collection efficiency and low impurity levels required.

#### Air Filtration Devices

High Volume Samplers. Originally, these devices was developed to monitor large volumes of atmosphere for radioactivity. Subsequently, it has been used to advantage to sample ambient for organic and inorganic pollutants.

As the name implies this device has the advantage of being capable of sampling a large volume of air in a relatively short period of time. However, it is customarily operated for 24 hours. During this period, the average sampling rate is 1.4 cubic meters per minute or 2016 cubic meters per 24 hours. Thus, with a high volume sampler ("hi vol" as it is called) sufficient pollutants can be collected for a variety of analyses.

The hi vol has a high particle collection capability. Commonly used with fiber-glass filter, it is possible to collect particles up to 100 micrometers under quiescent conditions. Wind turbulence, however, will allow collection of larger and heavier solids.

When considered carefully, this sampling method is of great value for a variety of purposes. The 24-hour samples can be used to report the day to day average pollutant levels. Seasonal variations may also be noted as, for example, the comparison of cold versus hot season data. Urban versus rural differences are also readily distinguished. But the use of such sampling periods reduces sample irregularities, precluding the gathering of daily cyclical information.

Low Volume Samplers. These filtration devices have had ample use in the air pollution-related field of industrial hygiene. As such they are capable of sampling relatively heavily contaminated atmospheres successfully in a short period of time, while incorporating desirable features including ease of operation, low initial and maintenance cost and some degree of portability. Their application to airborne trace-metal studies has been somewhat limited because the insensitivity of available analytical methods has prevented determinations on very small samples.

Tape Samplers. The tape sampler is an automatic sampling device which was developed to evaluate the soiling potential and the visibility qualities of the ambient atmosphere. It consists of a vacuum pump, a sampling nozzle, a timing circuit and a cellulose filter tape. In operation

the vacuum pump draws the ambient air containing suspended particulates through the cellulose filter tape held in the sampling nozzle. The particulate matter is then deposited onto the filter tape. At pre-determined intervals the tape is advanced automatically and another sampling period is begun. As many as 600 sample spots may be collected on the 100 feet rolls of filter tape.

The sampling period may be selected by setting the desired interval on the automatic timer. The time sampled per spot may be varied from ten minutes to as long as  $3\frac{1}{2}$  hours in ten minute increments. The rate of flow of sample air through the instrument is usually in the neighborhood of seven liters per minute. The sample is drawn through a circular spot one-half to one inch in diameter.

From the versatility of the tape sampler it can be seen that there are numerous advantages to its use for air pollution sampling. The wide variations of sampling periods which may be selected allows using this device to meet the particular need of many sampling programs. In addition, the large number of samples which can be obtained per day permit detecting short-term variations in pollutant levels. All of this can be done with a minimum attention given to the instrument as the sampling is performed automatically.

Although, as mentioned earlier, the tape sampler has been used primarily to measure visibility coefficients, some workers have performed chemical analysis of the sample spot in order to determine selected trace substances. Using a Whatman 4 filter tape, MacLeod and Lee [38] determined the concentration of airborne Cu, Pb, and Cd from two-hour samples collected with a spot tape sampler. Additionally,



West [39-41] has developed numerous semi-quantitative methods for the determination of Fe, Cu, Ni, Pb, Zn, Cd, and others, via the ring-oven technique which, he claims, are applicable to samples taken with an automatic tape sampler.

## CHAPTER III

## ANALYSIS OF ULTRATRACE METAL SAMPLES

The determination of the concentration of an atmospheric pollutant is an essential requirement in defining an air pollution problem, whether the aim of the analysis is to establish background level concentrations for legislative purposes, to measure the effectiveness of control equipment, to determine the levels of concentration damaging to vegetation and animals, or to determine the effect of air pollution on the health of people or animals. The analytical requirements are not likely to be identical for each of these aims; consequently a variety of procedures may be needed to study even a single pollutant at various levels of concentration. In cursory investigations, a quick answer is often possible by the use of simple methods and a minimum of special equipment. But in comprehensive examinations or when it is necessary to identify an unrecognized pollutant or when the levels of known pollutants fall into the trace or ultra trace (ppm and ppb) analysis, as it is most commonly the case with metal aerosols, the solution is more difficult and requires the application of specialized techniques and of instrumental analysis.

As was discussed in the previous chapter, an analysis and the conclusions which can be drawn from it will have significance only when certain requirements are satisfied. These requirements include the control of the sampling-analytical set-up and imply that the overall

efficiency of the sampling method is known, that a sufficient amount of impurity has been collected to permit a choice of a method for the desired concentration range, and that the analytical method chosen possesses satisfactory sensitivity and reliability. In addition, it must always be kept in mind that in the analysis of real samples, the final result is the product of a multistage process, each step of which is an input channel for error. Thus, careful consideration should be given to all potential sources of contamination and/or variability. This section discusses the sources of error in the detection and determination of trace metals, and the common instrumental methods employed in the analysis.

#### Sources of Errors in Ultra Trace Metal Analysis

Obtaining a high degree of accuracy and reproducibility in the analysis of ultra trace metals is a task that requires a conscientious effort to control the potential error sources commonly encountered in this delicate type of analysis. Because of the minute quantities of metals involved with any given sample, the number of factors that will affect a method or a measurement is enormous. The major ones are usually obvious, so we are aware of them and can attempt to control or avoid them. Some factors vary so little or so rarely in the working environment that they are easily overlooked or else the trouble goes away before there is enough time to figure out what was causing it. Many factors are actually quite significant, yet their influence is difficult to detect simply because a situation that reveals their effect has been never encountered. In this respect, laboratory intercomparisons

can prove to be of value.

As a general rule one can divide the sources of errors in terms of whether they will affect primarily the accuracy or the precision of the analysis. One would expect, for instance, that the impurities introduced by reagents, apparatus and laboratory air would mainly affect the precision, while adsorption and volatilization of the sample would tend to affect the accuracy. The magnitude of the individual errors will, of course, differ from element to element, and from one sample opening procedure to another, so that one can only examine the sources of errors in general and then attempt to control them by available means which are relevant to the method of analysis.

#### The Laboratory

Special standards of cleanliness must be maintained in laboratories where ultra-trace metal analysis is to be performed. In addition to the particularly common metallic elements in air, such as Al, Fe, Ca, Na, K, Mg and Ti, the atmosphere of heavily populated areas also contains less common elements including Pb, V, Zn, Ni, Cr, and Cu at concentrations above  $0.1 \mu\text{g}/\text{m}^3$  [42,43]. The dust in laboratories may also contain many unusual elements at low levels, depending on the type of work being carried out. Thus, Ag, Au, Ga, In, Tl, Bi, As and Sn have all been found in relatively high concentrations [44]. The sources of these impurities, which should be sought both outside and inside the laboratory, include building and industrial dust, rust, and exhaust fumes from motor vehicles and factories. Microparticles of the most diverse composition may be derived from the wear on floors, walls and ceilings, from clothing

and from the skin of persons working in the laboratory. Air dried healthy skin, for instance, has been shown to contain typically about 6 ppm Zn, .03 ppm Ag, .77 ppm As, and 2 ppb Au. [45]. Traces of Zn can also be derived from cosmetics and white paper.

Corroding constructional materials considerably increase the levels of Fe, Cr, Ni, and Mo, and increased levels of Cu and Zn may be traced in many cases to heating equipment such as water-heaters, steam baths, sand baths and gas burners and to common laboratory cleaning items, such as paper towels. Detergents and other cleaning materials introduce Na and Mg, while trace organics left may heavily complex metals such that certain analytical techniques are rendered inaccurate.

There are several steps which can be taken to maintain the sample as free as possible from laboratory contamination. A simple and inexpensive approach, was used throughout this work. It consisted of keeping sample handling to a minimum while making certain that all glass or plastic ware that came into contact with the sample had been acid-leached and properly protected from the lab environment. Parafilm type paper was used to cover any material which had to be isolated. Other alternatives include the use of plastic glove-boxes which can be flushed with purified air or with an inert gas and thus help reduce the contamination considerably. In addition, instead of working in the open laboratory for the dissolution of samples or the evaporation of solutions, completely sealed vessels can be used [46], or the whole analytical procedure can be performed in a closed system where the sample is protected from contamination during all stages except during the transfer into the system.

When necessary, even more stringent purity conditions can be achieved with the use of high capacity air filters. These type of filters allow whole rooms to be maintained substantially free from dust and suspended particles. Such "clean rooms" are flushed by a laminar flow of clean air and may be entered only through air-locks, while wearing special dust-free protective clothing.

Alternatively, a "clean bench", that is a hood which works on the principle of laminar flow using the high capacity air filters, can provide small contamination free areas in a laboratory. Such benches are less expensive to acquire and operate.

#### Exchange Process Between Solutions and Vessels

The exchange processes that may occur between solutions and vessels can be a significant source of chemical variation in a sample especially when the concentrations are below  $1 \times 10^{-3}$  M. This variation results from the adsorption and desorption exchange reactions taking place at the irregular surface of vessels. Although the amounts involved in the processes are extremely small it must be realized that when dealing with extremely dilute solutions rather significant changes in concentration can result. The factors that affect the exchange processes between solutions and vessels will be considered below.

Adsorption. Very few measurements on the adsorption of ions from aqueous solutions on to surfaces commonly used for trace analysis can be usefully compared, since a multitude of parameters such as container material, nature of ions, concentrations, pH values, other ions present, contact time and the manufacture and pretreatment of the surface, all complicate the investigations. In addition, the processes

of ion-exchange has to be considered. In many cases the effects decrease for the following sequence of materials: borosilicate glass, soda glass, platinum, silica, polyethylene, polypropylene, and Teflon [47-49]. Posselt and Weber [50] for instance, have observed that at  $\text{pH} > 7$  the loss of  $\text{Cd}^{2+}$  to borosilicate glass is more severe than to other types of material, and that Teflon, polyethylene and polypropylene have the lowest adsorptive properties with regard to the cadmium aqueous species. But there are many exceptions. For example, for  $\text{Cd(II)}$  solutions ( $2 \times 10^{-5}\text{M}$ ) increasing absorption was found, in the sequence silica, Teflon, polyethylene, glass, at  $\text{pH} 9$ , but at  $\text{pH} 1.5$  silica absorbed more strongly than Teflon [51]. Studies with  $\text{Zn(II)}$  under the same conditions and at the same concentration showed adsorption increasing in the sequence Teflon, polyethylene, silica, glass at  $\text{pH} 9$ , whereas at  $\text{pH} 1.5$ , silica adsorbed more weakly than polyethylene.

The dependance of the adsorption on the nature of the ion may be gathered from the following examples: a)  $\text{Pb(II)}$  and  $\text{H}^+$  are more strongly adsorbed on glass than  $\text{Cu}^{+2}$ ,  $\text{Ba}^{+2}$ , and  $\text{K}^+$ , [52]; and b) long term studies on aqueous ions of Sc, Fe, Co, Pb, Ag, In, Sb, Cs, U, and Sr have shown differences in their behavior toward polyethylene and glass [53].

There are several measures which can be taken to minimize the loss of trace metals due to adsorption. One could, for instance, work exclusively with laboratory ware made from Teflon, which seems to be the best overall material. But this alternative, besides being

expensive, its impractical and many times unnecessary. Borosilicate glassware can be used without appreciable loss of trace metals if certain precautions are taken. In this study the treatment of glassware with concentrated nitric acid and with dilute (.1M) nitric acid for several days, followed by rinsing with copious amounts of reagent grade type I water gave excellent results. The particular effectiveness of this acid treatment has been attributed to the strong bonding of hydrogen ions to glass surfaces [52]. Because the pH affects the adsorption rate, solutions prepared in borosilicate glass volumetric flasks were kept at a pH of one or below. This acidification procedure is then recommended for the analysis of trace heavy metals, as a mean to prevent precipitation and adsorption of the metals on the walls of borosilicate glass bottles.

Desorption. Since neither completely pure nor completely inert materials are known, great difficulties are encountered in the preparation and storage of acids, alkalies, solutions of complexing agents, and high purity water, without introduction of contaminating residues from the materials of the container. The desorption effect becomes more noticeable by long storage so that this factor further increases the errors in trace analysis. As in the case of adsorption, the experience with desorption is limited as the procedures used depend on the particular reagent being investigated.

For long term storage of reagents, only vessels of quartz, Teflon, polyethylene or polypropylene should be used [54]. Results are available from long term studies on these materials exposed to



hydrofluoric, hydrochloric and nitric acids, and also to pure water [55]. Twenty-two elements were sought spectrographically. The levels of twelve were below the limits of detection (Bi, W, Ga, In, Au, Ag, Mo, Sn, Sb, Tl, Ta and Zn). The amounts of Al, Fe, Ca and Mg in the acids stored in Teflon and polyethylene vessels changed very little during thirty days. Nitric and hydrochloric acids took only a very small amount of Mg from silica. When high-purity water with Ca, Mg, Ti, and Cu contents in the range of  $10^{-7}$  to  $10^{-10}$  percent was stored in Teflon or polyethylene for thirty days, these levels increased by a factor between five and ten, and in addition small amounts of Al, Fe, and Cr were found. After prolonged storage, only the concentrations of Cr and Cu showed any further increase. It follows, then, that water remains pure only when stored for short periods of time.

The advantageous adsorption and desorption properties of high-pressure polyethylene (low pressure polyethylene is entirely unsuitable) and Teflon towards inorganic ions should not be allowed to obscure the fact that other type of interferences may be introduced. Polyethylene specially, even after suitable treatment, releases organic reducing agents which may affect ions in higher oxidation states. Impurities found in solutions that have been kept in polyethylene sometimes cause interferences in ultraviolet spectrometry [56], and in many electrochemical analysis [44]. Teflon, as manufactured, is usually very low in trace metals, but in the process of fabrication into chemical apparatus particles of grit, rust, and dirt may become embedded in the surface to act as a source of contamination for long periods of time.

## Reagents

In ultra trace analysis of metals, the greatest care and attention must be paid to the reagents used, as the degree of purity obtainable varies very much from one reagent to the other, and from element to element. The widely used analytical reagent grade chemicals are seldom suitable for this analysis without some purification scheme by which the levels of commonly encountered contaminants, such as Mg, Al, Ca, Mn, Fe, Ni, Cu, and Pb as well as other less common elements, be reduced to around  $10^{-7}$  to  $10^{-9}$  percent. The only way to be sure of the purity of a reagent is by checking it regularly, and therefore it is best whenever possible, to use only a few easily purified reagents such as HCl, HNO<sub>3</sub>, HF, NH<sub>4</sub>OH, NH<sub>4</sub>Cl, and some organic solvents. In certain cases it may be sufficient to remove only a few interfering impurities; special purification procedures may be devised based on distillation, electrodeposition into a mercury pool, passage through a chelating resin, etc. In addition, the preparation of reagents in a dust-free atmosphere may reduce the contamination levels by more than one order of magnitude.

In recent years, high-purity reagents having trade names such as "Aristar" (B.D.H.), and "Ultrex" (J. T. Baker) have become available. Although they do not satisfy all standards required for ultra-trace analysis, as the control of impurities is restricted to certain elements, our experience with Ultrex Chemicals has indicated excellent reliability and purity for polarographic work. However, it is often difficult to maintain the original high level of purity. In order

to keep a high purity, borosilicate glass bottles, shown in Figure 1, were used in this study. After an extensive acid pretreatment, the bottles safely stored concentrated Ultrex  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{NH}_4\text{OH}$ . The hollow stopper was used as a reservoir to dispense chemicals without contaminating the rest of the reagents.

Another major problem is the storage and stability of very dilute standard solutions. The best storage conditions should be determined beforehand. In addition to the phenomena of adsorption and desorption, the effect of exposure to light and to heat should also be considered. It is advisable to keep relatively concentrated stock solutions, and to dilute them by using calibrated pipettes and standard volumetric flasks immediately before use. The surface of all the apparatus should be equilibrated with the solution by shaking or allowing to stand overnight with a portion of the solution, discarding that portion, and filling up with the remaining portion for storage and use. It is a good practice to use the same apparatus for solutions of the same concentration as the apparatus is then permanently equilibrated.

#### Sample Digestion Methods

Most techniques commonly employed for the determination of ultra trace metals in particulate matter require that the sample be brought into solution. Many different decomposition methods are used; the better ones being those which can provide within a relatively short time a digested sample ready for analysis, with a minimum of both sample loss and introduction of impurities.

Since filtration is the most widely used sampling method, the

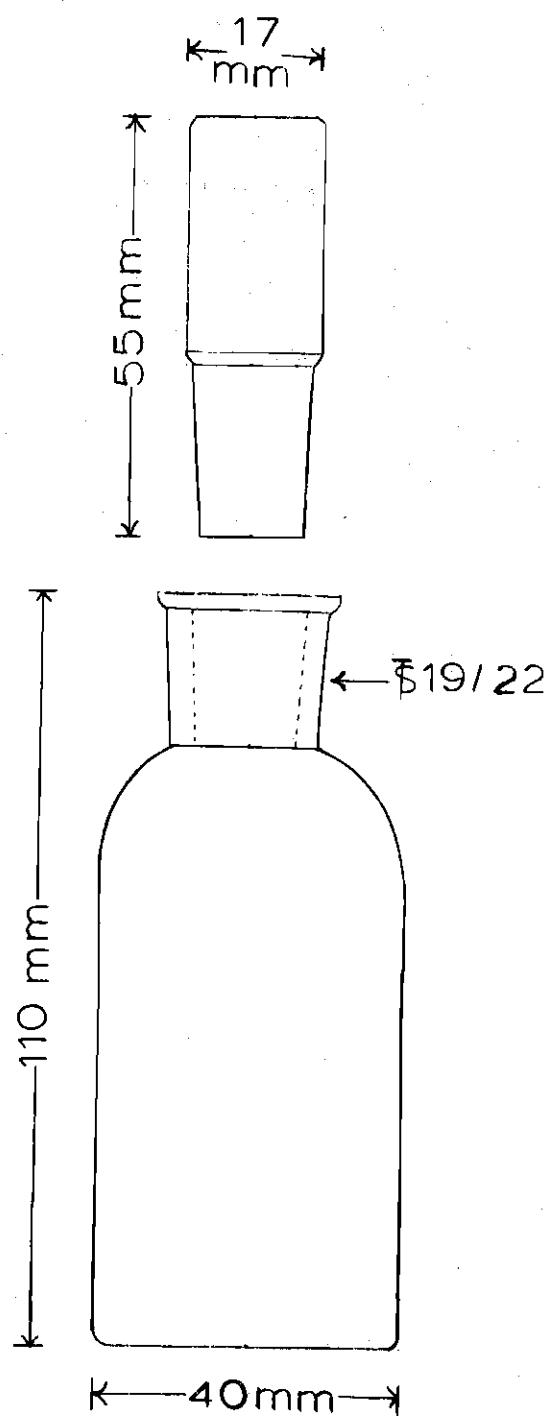


Figure 1. Reagent Storage Bottle. Hollow stopper serves as a reservoir to dispense reagents without contamination.

digestion method has to deal with the removal of the particulate matter from the filter medium. In the case of glass-fiber filters, acid extractions [57] seem to be most commonly employed although occasionally some workers have dissolved the complete filter with the use of hydrofluoric acid [58]. However, fiber glass filters contain an extremely high level and great variety of impurities and total dissolution only increases the already high metal background. More commonly, organic filter media such as cellulose and its esters are used for ultra-trace metal analysis. Since these can be readily dry ashed, ashing for matrix decomposition is preferred. The oldest and most simple method of dry ashing, heating in a muffle furnace at 400-800°C in the presence of air, can lead to loss of many elements, including Hg, Pb, Zn, Cd, Ga, In, Tl, Sb, Fe, Cr, and Cu [60]. The addition of fluxes such as sulphur, phosphates, or sulfuric acid, reduces the losses in many cases, but magnifies the risk of raising the blank value. Interaction between the fluxes and the vessels, such as formation of insoluble silicates from silica and porcelain, and the formation of insoluble oxides, causes losses which, together with the other disadvantages, render these procedures unsuitable for ultra trace metal analysis. Better conditions for ultra-trace analysis are offered by "low-temperature ashing" [59]. In this procedure the sample is burned in a stream of oxygen at a pressure of 2-5 mm Hg, within a high frequency field of 300 W at 13.56 MHz, at temperatures between 100 and 200°C. Compounds of Ag, Au, Hg, and Se, still volatile at these temperatures, may be trapped in a suitable receiver.

The dry ashing step is then followed by a simple dissolution of the residue in acid [38], or by a thorough decomposition in a Teflon bomb [61,62] if a high silicate content is suspected. The disadvantage of using low temperature ashing is the long period of time, (anywhere from two to 14 hours depending on the number and size of the samples) required for the complete decomposition of the organic matrix.

Another decomposition method commonly used to digest particulate-matter samples is the wet ashing method. The sample is brought into solution with the use of sulfuric, nitric, or perchloric acids, or various mixtures of these. The temperatures for wet ashing are low compared to dry ashing but loss of Se, Hg, Au, Fe and other metals has been reported [63]. For this reason ashing under reflux has been recommended. The wet-ashing method has some advantages in that it does not require as long periods of time for completion as does low temperature ashing but care must be exercised in the selection of the acid mixtures since only a limited number of reagents are available with the degree of purity necessary. In addition, this procedure requires constant attention and temperature control in order to avoid accidents and sample loss. For more detailed information on the techniques of wet and dry ashing, the work of Pijck, Gillis, and Hoste [64] should be consulted.

As an alternative to complete filter destruction several authors have examined the feasibility of using a simple filter metal extraction with a suitable medium as a mean to bring the sample into solution. West et al. [39-41], have developed numerous methods for the semi-quantitative determination of metals in air samples taken on Whatman 41

filter paper. These workers employ nitric or hydrochloric acids, in various concentrations, for the extraction step. In their work, Fe, Cu and Ni have been extracted with 3M HCl [39]; Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn with 0.1 M HCl [40]; and Pb with 1M HNO<sub>3</sub> [41]. Jernigan, Ray and Duce [65] have also used an acid extraction, in combination with an ultrasonic sample removal, for the determination of lead. Thus, a filter sample and the eluting acid (0.1M HNO<sub>3</sub>) were placed in a Branson ultrasonic cleaner for ten minutes to remove the particulate matter from the filter. The study showed that by ultrasonic cleaning 98 percent of the material is removed after five minutes and that longer cleaning times produced no variation in the amount of Pb extracted. Janssens and Dams [66] confirmed the high efficiency of the combined acid and ultrasonic extraction by comparing results with low temperature ashing; no statistical difference was found between the results of the lead concentration in a Whatman 41 filter sample using these techniques. They further explored the dependence of lead recovery on the acidity of the solution and found 0.1 M HNO<sub>3</sub> offered the best compromise between quantitative extraction and high sensitivity. On the other hand, distilled water was not effective in completely removing the lead from the filter.

From the digestion procedures examined it seems that the last one, the combined acid and ultrasonic extraction, provides the fastest, highest efficiency method for bringing a particulate matter filter sample into solution. While it can be contended that in real sample analysis there may be sample loss due to the insolubility of certain

metallic compounds under such relatively mild extraction conditions, one is forced to wonder if total sample destruction techniques are truly relevant to air pollution work, where the interest lies not in the total amount of metals, but in the amount that can be readily assimilated by the body under its own mild digestion conditions. Therefore, the acid and ultrasonic extraction technique was chosen for the digestion step in this work. It provided the additional advantage of allowing the multiple sample extractions necessary when analysing a large number of samples.

#### Instrumental Methods of Analysis for Airborne Metals

In order to measure at the parts per billion level of metal aerosols commonly encountered in air pollution studies, methods of high sensitivity and selectivity are needed. They must be applicable to real-world samples, be accurate and reliable, and preferably should also be convenient and economical. According to the literature there are several instrumental methods which meet most of these essential requirements to varying degrees.

#### Atomic Absorption Spectrophotometry

One of the methods which has enjoyed increased popularity for the analysis of a variety of metals in atmospheric particulate matter is atomic absorption spectrophotometry (AAS). Several investigators have used AAS to measure a number of metals in air samples collected from different locations [67-69]. Hwang [70] has extensively reviewed the use of various AAS procedures to measure trace metals in air. In addition, a number of investigators have developed procedures which



avoid or minimize problems such as high blank background, incomplete digestion and sample volatilization, which tend to limit the applicability of AAS. Kneip [34] has described a procedure using glass fiber filters, low temperature ashing, and leaching the samples with nitric acid for the determination of eight metals in atmospheric particulate matter. Thompson [71] has described a similar procedure where the sample is leached with HCl and  $\text{HNO}_3$  and as many as 13 metals can be measured. Kometani [60] has described a procedure involving the collection of particulate matter on S&S paper filters, the addition of  $\text{H}_2\text{SO}_4$  to convert possible volatile metal salts to the relatively nonvolatile metal sulfates, followed by a dry ashing step at  $500^\circ\text{C}$ , and the dissolution of the remaining material in  $\text{HF-HNO}_3$ . This author has used his procedure to determine ten different metals in particulate matter in New York. Hwang and Feldman [72] have described the use of membrane filters to minimize blank problems when measuring the atmospheric concentration of Cr, Ni, Mn, and Cu. Janssens and Dams [66] have used nonflame atomic absorption spectroscopy (NFAAS) for the determination of lead. In their work a Whatman 41 filter sample was subjected to ultrasonic vibration while submerged in  $0.1\text{M HNO}_3$  to remove the particulate matter followed by determination by NFAAS with a Massmann oven.

#### Neutron Activation Analysis

Neutron activation analysis (NAA) method is probably one of the most sensitive analytical tools available to the analyst and depends on the artificial production of a radioactive isotope and the subsequent counting of its disintegrations. The method is relatively

free from interferences because of the unique character of the decay periods of the isotopes and its broad applicability may be appreciated when it is considered that more than 700 isotopes have been identified for known elements. NAA offers the additional advantage of being nondestructive and able to analyze many environmental samples directly, although in certain cases extensive sample pretreatment and radiochemical separations may be required in order to enhance the sensitivity. Since activation sources at the present are quite expensive, a wider use of the technique will depend on the development of less expensive sources.

The wide range of applications of NAA to the determination of trace metals in air may be derived from the work reported by some investigators. Kuykendall, et al. [73] collected particulate samples from the metropolitan area of Cleveland, Ohio on Whatman 41 filters by operating a high volume sampler for 24 hours. After irradiation of the sample the analysis for 36 elements, including Ti, Cu, V, Fe, Cd, Zn, Ni, Co, and Hg was performed by counting the short and long lived activities with a Ge (Li) detector coupled with a multi-channel analyzer. Schramel et al. [74] reported the determination of 12 selected microelements including As, Cd, Cr, Cu and Zn in air particles by NAA combined with a radiochemical separation technique.

#### Emission Spectrography

Emission spectrography (ES) is widely used to establish the elemental composition of mixtures and is indispensable for the exploratory examination of particulate matter. It has a wide range of applications since of the known elements, about 70 can be

determined by ES with various degrees of sensitivity. Depending on the aim of the investigation and the amount of material available, this analytical tool can be employed to perform qualitative, semi-quantitative and quantitative analysis. Keenan and Byers [75] have reported a semiquantitative method for 21 elements in particulate matter collected on a glass fiber filter with a high-volume sampler. The entire filter was digested first with acid. Then, graphite rods impregnated with the digested solution were exposed in a dc arc over three different regions to cover the desired spectral range. Quantification was obtained by densitometric comparisons of the characteristic spectral lines with similar lines for graded standard solutions of the elements investigated.

Other comprehensive ES analysis of aerosols and settled dust are described by Cholak et al. [76-78]. In the investigation, a variety of ES methods combining chemical separations and concentrations with a special excitation technique were used to improve the sensitivities of detection for various elements. An acid digest of the particulate matter was subject to a dc arc over graphite rods. Determined from a single exposure were Al, Cu, Fe, Pb, Mn, Ag, Sn, Ti and V, while portions of the sample were treated separately to determine As, Be and Cd.

#### Polarography and Anodic Stripping Voltametry

Polarography and its advanced technique of anodic stripping voltammetry (ASV) have earned acceptance during recent years as a valuable analytical tool for the determination of metals in particulate matter. Polarographic methods for measurements of lead in air

have been published by Levine [79] and by Dubois and Monkman [80]. However, the majority of current literature establishes the more sensitive ASV as the electrochemical technique of choice. ASV has been reviewed by Neeb [81] and some applications to the analysis of air samples have been given by Matson [82].

One of the reasons why ASV has increased in popularity among researchers is that besides the enhanced sensitivity, it shares with classical dc polarography the capability for multielement analysis. For a reasonably small investment, simultaneous analysis of various cations, including determination of their valence states, can be performed, thus eliminating lamp changes and recalibration inherent in multielemental atomic absorption spectroscopy (AAS). The increased operator skill required for ASV over AAS is a potential deterrent, but as the demand for ultra-trace contaminant analysis increases, spectrophotometric techniques will require comparable skill.

Analysis of metallic aerosols has been described by several investigators. Harrison and Winchester [57] determined the area wide distribution of Pb, Cu, Cd and Bi in 24-hour samples collected on glass fiber filters at 50 stations throughout the southwestern shore of Lake Michigan. The procedure consisted of digesting a  $13 \text{ cm}^2$  portion of the filter with perchloric acid while heating to  $300^\circ\text{C}$  for  $\frac{1}{2}$  hour. After dilution with water the samples were allowed to stand for two days before determination by ASV with a thin Hg film wax impregnated graphite electrode. Colovos, Wilson and Moyers [61] described the application of ASV, with a hanging drop mercury electrode, (HDME) for

the determination of Zn, Cd, Pb and Cu in airborne particulate matter collected on Millipore filters. The samples were wet with 0.1 M  $K_2SO_4$  and ashed in a high vacuum, low temperature asher. Dissolution of all inorganic matter was achieved by digestion with nitric and hydrofluoric acid in a Teflon bomb. After evaporation to dryness, the residue was dissolved in 0.1 M  $KNO_3$  and subjected to ASV analysis, plating at -1.2 volt. Colovos et al. [22] used this procedure, combining ASV with atomic absorption spectrometry, to determine the concentration of Pb, Cd, Zn, Cu, Ca, Fe, Mg, Mn and Al in metal aerosols. Cohen [83], Wahdat and Neeb [84], and Glodowski et al. [85] have also described procedures for the analysis of metal aerosols by ASV.

Other workers have advantageously used the high sensitivity of ASV to increase the sampling frequency and thus obtain time variations of the concentration of airborne metals without sacrificing reliability and reproducibility. Harrison, Matson and Winchester [86] sampled aerosol particles for two hour periods for over a 42 hours time interval using a modified seven stage Andersen cascade impactor and a glass fiber backup filter. On each of the stainless steel Andersen impactor plates was placed a four mil thick polyethylene disc on which samples of different size fractions were obtained. The discs were then placed in a quartz cell with 0.1 M NaCl and the sample was removed by ultrasonic agitation, which proved to be 90-97 percent efficient. The sample was then analyzed on a multiple plating anodic stripping apparatus using a composite mercury graphite electrode. MacLeod and Lee [38] applied ASV to two hour samples collected on

Whatman 4 filter with a tape sampler. The sampled spot were analyzed for Pb, Cd, and Cu after ashing at low temperature and extracting with 1:1 perchloric-nitric acid solution. A limitation of this method pointed out by the authors was the high background level of metals in the Whatman 4 filter tape. This fact prevented examination at shorter intervals and restricted the detection limit of the technique.

#### Other Methods

Other instrumental methods which can be used for the determination of metals in air include X-ray fluorescence, mass spectrometry, and gas chromatography. Dulka and Risby [87] have reviewed recently some of these methods and their application to ultra-trace analysis of metals. They include a fair presentation of the detection limits of several instrumental methods of analysis for different metallic elements.

## CHAPTER IV

## THEORY

Classical (DC) Polarography

Polarography is an electrochemical technique in which potential is applied to a small electrode and the resulting cell current measured. As a potential is reached at which an electron transfer reaction can occur, the cell current increases. The increase in current is limited by the rate at which the reactant can diffuse to the electrode surface and hence is proportional to the concentration of the reacting species in the bulk of the solution. Further increases in potential do not yield further increases in current until a potential is reached at which another electron transfer reaction can occur. The result of a polarographic experiment, called a polarogram, is a display of cell current on the ordinate and electrode potential on the abscissa. The potential at which a current increase, that is, a wave, occurs is used to identify the particular electron transfer reaction, and the amount of current increase in the wave is used to determine the concentration of reactant.

The potential at which the current has increased to one half of its maximum for a wave, is called the half-wave potential,  $E_{1/2}$ . The shape of the polarographic wave is given by:

$$E = E_{1/2} + (RT/nF) \ln[(i_d - i)/i] \quad (2)$$

where

$$E_{\frac{1}{2}} = E_o - (RT/nF) \ln(D_o/D_r)^{\frac{1}{2}} .$$

Equation 2 results from the combination of the diffusion equations for the electrode process with the Nernst equation. In Equation 2, R is the gas constant, T the absolute temperature, F the Faraday, n the number of electrons transferred in the electrode reaction, and i the current at any point on the rising portion of the wave.  $D_o$  and  $D_r$  are the diffusion coefficients for the oxidized and reduced species in the half reaction.

Early attempts to utilize diffusion-controlled processes for analysis led to erratic results because of day to day changes in the condition of the electrode surface. Heyrovsky [88] introduced the use of the dropping-mercury electrode (DME) which gives reproducible results because the mercury drop is periodically replaced, thus giving a fresh, uncontaminated surface at which the reaction can occur.

The DME consists of a length of fine bore capillary tubing connected at one end to a reservoir of mercury. The other end of the capillary tubing dips into the cell solution. Mercury from the reservoir flows slowly through the capillary forming a drop electrode at the solution end. This drop grows slowly until it falls and is replaced by a new growing drop. It is now common practice to dislodge the drop at a preset time by striking the capillary with the armature of a solenoid. This eliminates variations in the drop time that result from changes in the mercury-solution interfacial tension



as the electrode potential is changed.

Starting from the Cottrell equation, which in turn is based on Fick's laws of diffusion, Ilkovic [89] derived the theoretical equation relating diffusion limited current at the DME to concentration:

$$i_d = 702nD^{1/2}Cm^{2/3}t_d^{1/6} \quad (3)$$

In Equation 3,  $t_d$  is the time (sec) between detachments of successive electrode drops (referred to hereafter as drop time).  $C$  is the concentration of reactant (mmoles/l),  $m$  is the flow rate of mercury (mg/sec), and  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{sec}$ ). The numerical factor 702 derives from constants and conversion factors.

The current varies as the electrode drop grows and is detached. The  $i_d$  of Equation 3 is the instantaneous current (microamperes) at the end of the drop life. Often, variations in the cell current are damped electrically, and in this case, the average current recorded is 6/7 of the maximum instantaneous current given by Equation 3.

Equation 3 was derived with the assumption that diffusion was the only process by which reactant was transported from the bulk of the solution to the electrode surface. In order to approximate this condition experimentally, it is necessary to add an inert salt (supporting electrolyte) to the cell solution. This supporting electrolyte minimizes transport of the reactant by electrical migration and also serves to decrease the ohmic resistance of the solution.

#### Limitations of DC Polarography

If the electron transfer current (DC-Faradaic current) discussed

above were the only source of current in the cell, it should be possible to amplify it electronically and achieve almost limitless sensitivity. However, there is another source of current in the cell which is independent of reactant concentration and acts to limit the sensitivity of DC Polarography. This other current is called the capacitance current or charging current. It arises from the fact that the interface between the mercury drop and the cell solution acts as a capacitor.

The capacitor requires current to charge the electrode to the desired potential. As the electrode drop grows, the surface area increases, the capacitance increases, and a continual flow of current is needed to keep the electrode at the desired potential. Furthermore, the capacitance is not a linear function of the electrode potential so the capacitance current varies as the potential is changed during the recording of a polarogram. In practice, the magnitude of the capacitance current is such as to obscure the Faradaic current when the concentration of reactant is significantly less than  $10^{-5}$  moles per liter.

A second limitation of DC Polarography is evident in solutions of more than one reactant species. If the species that reacts first, as the electrode potential is varied, is of equal or lower concentration than the species that reacts second, no particular problem exists. However, if the second species is much lower in concentration than the first species, it is very difficult to accurately measure the diffusion current due to the second species. For example,  $10^{-5}$  molar Cd(II) can be determined with reasonable accuracy if present alone in the solution. However, in the presence of  $10^{-3}$  molar Pb(II),  $10^{-5}$  molar Cd(II) is

almost undetectable by DC Polarography.

### Modern Variants of Polarography

A number of variations of polarography have been developed in attempts to overcome the limitations discussed above and, in some cases, to reduce the time required to obtain a polarogram. Tast and AC polarography have been discussed by Hayman [90]. In this section, a brief discussion of square-wave and pulse polarography will be presented.

### Square-Wave Polarography

When the potential of an electrode is changed abruptly by the application of a pulse, capacitance current flows until the electrode is charged to the new potential. The current flow is large at first and rapidly decays in accordance with Equation 4

$$i_c = (\Delta E/r) \exp(-t/rc) \quad (4)$$

In Equation 4,  $r$  is the cell resistance,  $c$  is the differential double-layer capacitance,  $t$  is the time after pulse application, and  $\Delta E$  is the magnitude of the potential step. If the potential step is relaxed (i.e. stepped back), capacitance current flows in the opposite direction. From Equation 4 it can be seen that the smaller the product,  $rc$ , the more quickly the pulse-capacitance current decays. In an electrochemical cell, the higher the concentration of supporting electrolyte the lower the resistance and the more quickly the pulse-capacitance current decays.

If the potential change discussed above takes the electrode to a potential at which an electrode reaction occurs, a pulse-Faradaic current will also flow. Under linear diffusion-controlled conditions, the pulse-Faradaic current is given by:

$$i_F = nFACD^{\frac{1}{2}}/\pi^{\frac{1}{2}}t^{\frac{1}{2}} \quad (5)$$

where  $n$ ,  $F$ ,  $D$ , and  $t$  are defined above;  $A$  is the electrode surface area in  $\text{cm}^2$ .

The total pulse current is proportional to the algebraic sum of the pulse-Faradaic and the pulse-capacitance components. From Equations (4) and (5) it can be seen the pulse-capacitance current decays as a function of  $\exp(-t/rc)$ , while the pulse-Faradaic current decays as a function of  $t^{-\frac{1}{2}}$ . Therefore, since the pulse-Faradaic current does not decay as rapidly as the capacitance component, after some time delay, the pulse-capacitance current becomes negligible as compared to the pulse-Faradaic current. At that time, the total pulse current is essentially equal to the pulse-Faradaic current; sampling at that time amounts to an almost complete rejection of the undesired pulse-capacitance current.

The rejection of the pulse-capacitance current, as described above, is the salient feature of square-wave polarography. In square-wave polarography, a small amplitude (usually  $<50$  mV) square-wave is superimposed on the usual DC electrode potential. The DC electrode potential is slowly changed so as to scan the potential region for the polarogram. Current is sampled after a sufficiently long time delay to allow the pulse-capacitance current to decay adequately.

Pulse-Faradaic current is plotted versus DC potential, and the polarogram has the same "derivative" form as those obtained by derivative-DC polarography and AC polarography.

Barker [91] derived the following equation for the alternating component of the current for a reversible electrochemical reaction

$$i = \pm \frac{n^2 F^2}{RT} \frac{C_b \Delta E}{(1+P)^2} \left( \frac{D}{\pi \tau} \right)^{1/2} \sum_{m=0}^{\infty} (-1)^m \frac{1}{(m+\beta)^{1/2}} \quad (6)$$

where

$$\beta = \frac{t}{\tau} \quad (0 < t < \tau)$$

and

$$P = \exp[(E - E_{1/2})nF/RT],$$

$E$  is the average potential during the drop life,  $E_{1/2}$  is the half-wave potential of the particular species of interest,  $t$  is the time elapsed from the beginning of the half-cycle, and  $\tau$  is the half-period of the square-wave applied.  $C_b$  is the concentration in the bulk of the solution and  $D$  is the diffusion coefficient of the electroactive species in consideration. This equation holds for only small square-wave voltages, i.e.,  $\Delta E \ll RT/nF$ .

From an inspection of equation (6) the amplitude of the alternating current is at a maximum when  $P$  is at a minimum value.  $P$  is minimum at the half-wave potential, known as the summit potential  $E_s$ , in techniques that yield derivative type polarograms. For reversible species, the width at the half-height of the peak for  $n = 1$ ,  $n = 2$ ,

and  $n = 3$  is calculated to be 90.4, 45.2, and 30 millivolts, respectively.

As has been pointed out recently by Sturrock and Carter [92] in their review of square-wave polarography, the limiting factor of this technique seems to be the DC-capacitance current. When analysis is performed with the dropping mercury electrode (DME) a DC capacitance current results from the fact that this current is a function of the electrode potential and of the changing area of the mercury drop. Thus the DC-capacitance current before pulse application will be different from that after pulse application. Since the differential measurement between half-cycles of the square wave does not subtract this DC-capacitance current, it acts as the primary factor limiting the sensitivity. However, this factor should vanish for a fixed area electrode, such as the hanging drop mercury electrode (HDME), used in this study.

### Pulse Polarography

Pulse polarography was first developed by Barker [93] as an outgrowth of his work with square wave polarography [94]. The main difference between these two methods lies in that in pulse polarography only one square-wave pulse is applied during the lifetime of a drop, whereas in square wave, a set of pulses is applied to the drop after a predetermined time.

There are three basic modes of operation in pulse polarography: normal, derivative, and differential-pulse polarography. The difference in the three techniques are due to differences in the applied potential before imposition of the voltage pulse, whether pulses are constant or increasing, and the currents recorded.

### Normal Pulse

At a predetermined time in the life of the drop, a square-wave pulse is applied for a duration of approximately 40-60 milliseconds. After the application of the pulse the potential returns to the initial potential (a ramp voltage is not applied). Then the next mercury drop is allowed to grow while a constantly applied initial potential is imposed on the electrode. At the same predetermined time a square-wave pulse of a little larger magnitude is applied. The current is measured during the last five to 20 milliseconds after the application of the pulse so that the charging current has decreased to a negligible value. To each succeeding drop a somewhat larger pulse is applied after which the potential is returned to the initial value.

The shape of the normal-pulse polarogram resembles an ordinary polarogram except the currents for identical concentrations of electro-active species are much larger.

### Derivative Pulse

The only difference in this technique and normal pulse polarography is the manner in which the currents are processed. In derivative pulse polarography a difference amplifier compares the current from successive drops and generates a voltage proportional to the difference. This produces a peak of approximately Gaussian shape, similar to the one obtained from square-wave polarography. Since the currents measurement is inherently more sensitive than the measurement of a plateau as in the normal mode, better resolution of the components is achievable with the derivative technique.

### Differential Pulse

In this method voltage pulses of equal magnitude but of less than 100 millivolts amplitude are superimposed on a slowly changing ramp voltage. Sampling occurs immediately prior to pulse application and again just before pulse relaxation. The difference between these currents is plotted as a function of potential and results in a curve similar in appearance to that obtained by derivative pulse polarography.

### Anodic Stripping Voltammetry

The procedure for anodic stripping voltammetry may be described as follows:

If the potential applied to a stationary electrode, such as hanging drop mercury electrode (HDME), is more negative than the half-wave potential of a particular reducible ion, then plating of the species on the electrode occurs. This plating step, called the "pre-electrolysis step" may be classified as either stoichiometric or nonstoichiometric depending on whether it is carried to completion or not. After this step, the deposited species are stripped anodically by sweeping the potential to more positive values. As the metal ions are returned to solution, a current peak occurs, the height of which is directly proportional to the concentration of the metal in the mercury. This step may also be either stoichiometric or non-stoichiometric. The two non-stoichiometric steps in succession are probably the most commonly employed combination in anodic stripping voltammetry (ASV), with a reproducible fraction of the reducible constituent being plated onto the electrode in the first step.

There is considerable improvement in the sensitivity with the



employment of ASV as compared to classical polarography, because the diffusion current to capacitance current ratio is larger. Thus, all modern variants of polarography benefit from this technique. However, the plating time, rate of stirring (if employed), and surface area must be carefully controlled in order to obtain reproducible results.

Although very sensitive, the ASV technique has some limitations and disadvantages. It cannot be employed for the determination of metals that do not form a mercury amalgam, e.g., chromium and iron. Another serious problem encountered is the formation of intermetallic compounds in the mercury which increases as the concentration of certain metals is increased in the amalgam. Interference of Ni with Zn and V with Cu [95] and depression of Zn by Cu and Ni as well as depression of Cd by Cu [96] has been reported for ASV. The problem of intermetallics are specially pronounced when a thin film mercury electrode (TFME) is used for the pre-electrolysis step. Because of the small volume of mercury and the large area of these electrodes, the concentration of the metals builds up to relatively large amounts which favor the formation of intermetallics. However, these problems are much less pronounced with the HDME, as was used in this study, because the relatively large volume of the mercury drop prevents the higher concentration build up the TFME allows. Laboratories which perform routine metal analysis in which this type of interference may be encountered usually employ calibration curves in which the concentration of the metal of interest is plotted versus the peak height of its wave for standard solutions of different interfering metal concentrations. Another step that may be taken to lessen this effect is to quantitate samples by means of a

standard addition technique which does not alter the molar ratios of the metals which form the intermetallic compounds. This way a "reproducible intermetallic formation" can be attained.

## CHAPTER V

## INSTRUMENTATION, EQUIPMENT AND REAGENTS

InstrumentationPolarograph

The square-wave polarograph used in this study was designed and built by the Chemistry Department electronics shop and has been described by Sturrock and Carter [92,97]. Several modifications were made to this instrument and are described below.

Sampling Delay Time. Previously, the transitions at each half-cycle of the square wave were used to initiate either a 400 or 800 microsecond delay. The delay time was modified to 1000 microseconds in order to allow a longer time for the pulse capacitance current to decay to a negligible value before the current measurement.

Computer Trigger. A computer-trigger pulse is generated from the integrator reset pulse (if the square wave is on and the mode switch is in the run position). This pulse allows the acquisition of data by the PDP-8 computer at the end of each square-wave cycle.

Integrator Pulse. Previously, the integrator reset pulse was disabled for the first two seconds of a four-second cycle. This avoided measuring currents during the early life of the mercury drop when working with the DME. For this study, a by-pass circuit was installed to allow a continuous integrator reset pulse and hence, a continuous computer trigger, necessary for HDME work.

### Computer

The computer used in this study was a Lab PDP-8e manufactured by the Digital Equipment Corporation. It consists of the central processor unit (CPU), 8192 words of 12-bit core memory, a 10-bit analog-to-digital converter (AD8-EA), an 8 channel analog preamplifier and multiplexer (AM8-EA), a point plot display control (VC8-EA), a real-time programmable clock (DK8-EP), a display oscilloscope (VR-14), a high-speed paper tape reader and punch (PC8-E), an X-Y recorder (HP7040A) and a teletype.

The multiplexer acts as a switching device so that more than one analog signal can be sampled and converted to digital representation by the analog-to-digital converter (ADC).

The digital clock of the computer is used to perform certain timing functions in the data acquisition process. The computer trigger pulse generated by the square-wave polarograph triggers one of the Schmidt Trigger inputs of the clock, which in turn, signals the computer via the interrupt line. The computer then starts sampling the cell current via the ADC. Each current measurement requires a computer trigger pulse such that, using a 30 Hz square wave, one integrated cell current sample is available to the computer for storage and handling every 16.7 milliseconds or every half cycle of the square-wave. From a maximum of 60 cell-current values per second, 50 of these are stored and summed together to achieve an averaging routine. The clock is then reset and started by a command from the computer which, after plotting on the display oscilloscope the average cell current value as a function of the cell voltage, is then forced to wait for 167 milliseconds such

that the total elapsed time for the sampling, averaging and plotting routine amounts to one second. After this delay the cycle starts all over again.

After the complete polarogram has been stored, the computer searches and reports the number of peaks, their locations, and heights. A hard copy plot can then be obtained from the computer through the interfaced X-Y recorder.

### Equipment

#### Polarographic Cell

A diagram of the polarographic cell is shown in Figure 2. It consists of a cell head made of 100 percent virgin Teflon, a 17 x 100mm propylene tube (Falcon Plastics No. 2018) or a 18 x 97mm Pyrex glass tube, a nitrogen gas bubbler (Penntube I special heavy wall, 0.016" I.D., 0.063: 0.D.), 10 x 3mm a magnetic stirring bar (Fisher Scientific Company No. F37119) and three electrodes which are described as follows:

Hanging Drop Mercury Electrode (HDME). A Beckman 39016 hanging drop mercury electrode assembly was used to extrude mercury drops of one microliter volume ( $1 \mu\text{l} = 0.0474 \text{ cm}^2$ ).

Reference Electrode. A Coleman 3-710 saturated-calomel electrode was modified to use in the polarographic cell. The modification consisted of fitting a piece of thin-wall Teflon tubing (Dixon Medical Products No. 736, .106: I.D. x 130" x 5") to a Vycor glass tip and connecting this to a saturated NaCl reservoir of the Coleman electrode. This procedure essentially extended the electrode probe deep down into

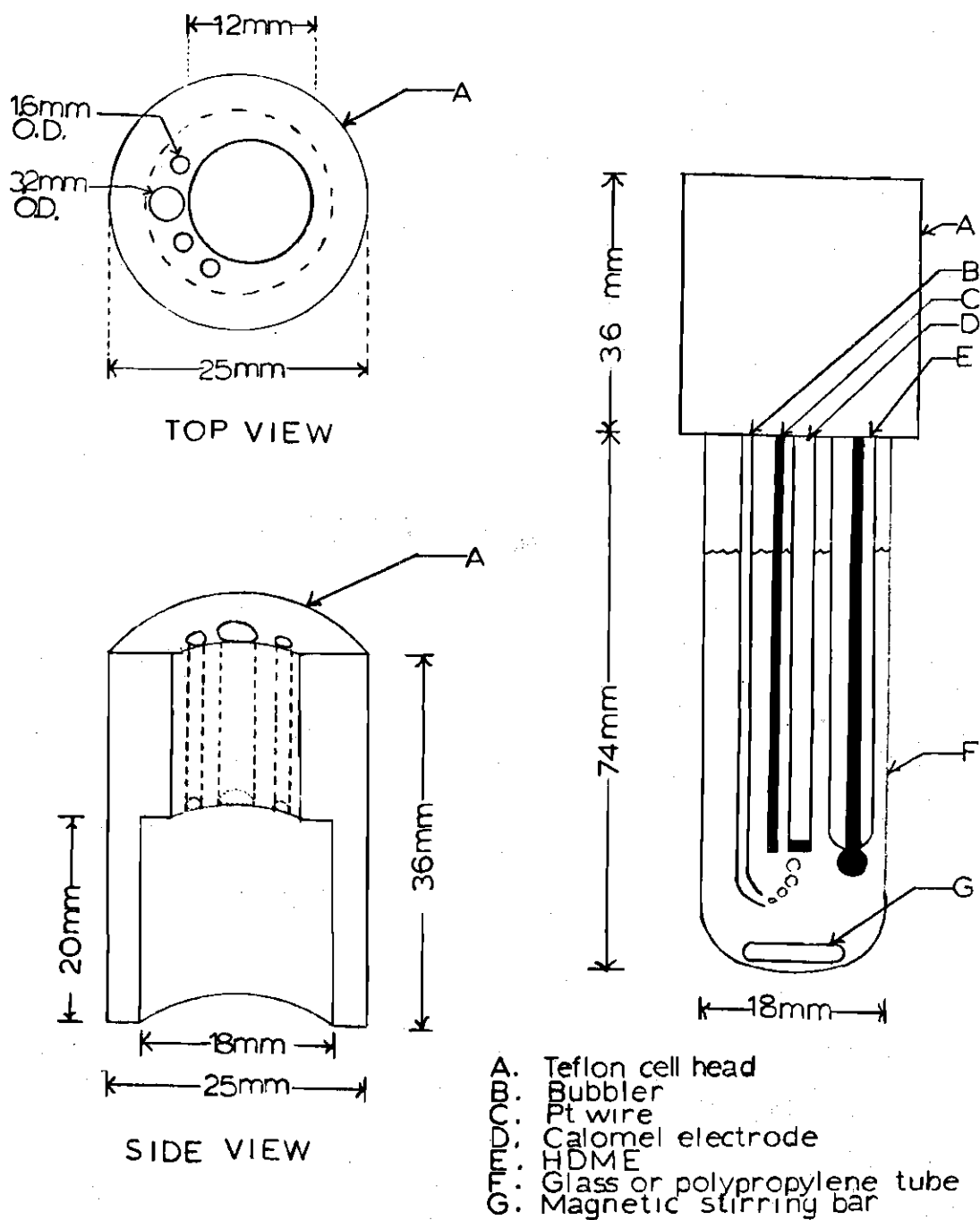


Figure 2. Polarographic Cell.

the polarographic cell.

Counter Electrode. The counter electrode simply consists of a platinum wire .038" diameter x 5" length.

In order to prevent metal contamination from the cell, all glass and plastic components are leached in concentrated, reagent-grade nitric acid for at least 24 hours and then rinsed with copious amounts of reagent-grade water.

#### Magnetic Stirrer

A Precision Scientific No. 65904 magnetic stirrer was used to stir the sample solution while plating into the HDME was effected.

#### Timer

The timer used to secure 150 seconds of plating time was a Precision Scientific No. 69230 timer.

#### pH Meter

pH measurements were made with a Corning Model 7 pH meter after calibrating the instrument with 0.05 F potassium acid phthalate.

#### Oscilloscope

A Tektronix Model RM 31a oscilloscope with a type H plug-in unit was employed for the monitoring of the various instrumental functions such as voltage, cell current, and the integrator output.

#### Recorder

A Hewlett-Packard 7004A X-Y recorder was used for recording the analog polarogram from the square-wave polarograph and the digital version from the PDP-8 computer was recorded with a Hewlett-Packard 7040A X-Y Recorder.

### Air Sampling Equipment

An A.I.S.I. tape sampler (Research Appliance Company 2301-SER) with built-in evaluator and recorder was used to obtain one and three hour-long particulate matter samples on Whatman 41 paper tape filter. This instrument was later modified to use with a higher capacity pump (Bell and Gosset Model LV) than the original equipment to permit sampling at 20 liters per minute. Additionally, a relay circuit which turned the pump off when the paper tape was advancing and an aluminum mesh filter support were installed in order to allow sampling with filter tapes having a smaller interfiber distance than Whatman 41.

### Ultrasonic Cleaner

The ultrasonic cleaner used for the extraction of filter samples was a Bronisonic model 42.

### Reagents

The reagents used in trace chemical analysis can contribute a large portion of the sample signal. For this reason it was necessary to carefully select and purify some of the reagents used.

### Water

Water exceeding the ASTM requirements for Reagent Grade Type I water was obtained by passing the water distilled from a Barnstead still through three mixed-bed deionizers (Cristal Lab FC-10) and then through a 0.2 micrometer flow-through filter (Gelman 12106). The water thus obtained has a conductance of less than 0.01 micromhos/cm.

### Nitrogen

The nitrogen gas used to deaerate the sample solutions was filtered



through a Millipore 0.45 micrometer filter supported by a Whatman 1 filter backing. When necessary, oxygen was removed either by the vanadous chloride method [98] or by passing through a high temperature furnace packed with copper (Sargent S36517).

#### Mercury

Bethlehem triple distilled mercury was purified by stripping anodically at +0.1 volts over 0.1M  $\text{HNO}_3$  (Ultrex) for at least three days.

#### 0.2M Ammonium Citrate Buffer

This buffer was prepared by dissolving 42.0 grams of citric acid (Certified A.C.S., Fisher Scientific Company A-104) in approximately 800 milliliters of reagent grade water and adjusting the pH to 3.2 with Ultrex  $\text{NH}_4\text{OH}$ . The volume was then made up to 1000 milliliters. Purification of this solution to concentrations below 1 ppb in all metals of concern was achieved through electrodeposition over a mercury pool at -1.4 volts for at least three days.

#### 0.1M Nitric Acid

This reagent was prepared by a 1/160 dilution of Ultrex  $\text{HNO}_3$  (J. T. Baker 4801) with reagent grade water.

#### Ammonium Hydroxide

Concentrated, Ultrex  $\text{NH}_4\text{OH}$  (J. T. Baker 1-4807) was used in all operations requiring the adjustment of pH.

#### Standard Metal Solutions

Standard stock solutions of copper, lead, and zinc containing 1000 ppm of the metals were prepared individually from commercial concentrated standards (J. T. Baker Dilut-It 4771, 4779, and 4799,

respectively). A 1000 ppm reference cadmium standard was obtained already prepared from Fisher Scientific Company, catalog No. SO-C-118. From each of these stock solutions a diluted stock containing 100 ppm was prepared. These diluted stock solutions were then used to prepare a combined metal standard containing between 1 and 20 ppm of the metals. This final standard was used to spike all samples and was prepared fresh daily. In preparing and diluting all standard solutions Ultrex 0.1M  $\text{HNO}_3$  was used instead of water to maintain a low pH, thus preventing the precipitation of the metals.

The samples were spiked with 10, 20, 25, 30, 50, 75 or 100 microliters of the spiking solution using a semi-automatic pipette system (Clay Adams 4700, 4701, and 4702).

All reagents were stored in Pyrex glass or polyethylene labware which has been thoroughly leached with concentrated nitric acid for at least 24 hours.

## CHAPTER VI

## EXPERIMENTAL RESULTS AND ANALYSIS

Determination of the Filter Blank

As was pointed out earlier, the total amount of metallic impurities in a blank may severely limit the application of an analytical method to an air pollution problem. This is specially true when attempting to determine short-time variations in the concentration of metal ions since a high blank value requires a large sample in order to allow differentiation between sample and blank. This factor, in turn, demands, in most cases, long-term sampling.

The contribution of reagents to the total blank impurity levels is an easier problem to solve nowadays since relatively metal-free reagents such as Ultrex  $\text{HNO}_3$ ,  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and many others are available. With the use of these, sample preparation and digestion can be accomplished with a minimum of contamination. In the case of the supporting electrolyte we used, ammonium citrate pH 3 buffer, the electrodeposition technique, proved to be both efficient and convenient as a means of metal removal. As shown in Table 8, the concentrations of copper, lead, cadmium, and zinc were limited to 1 ppb or less through electrodeposition over a mercury pool.

A more difficult task was to obtain a filter paper suitable for air sampling, yet with low enough impurity levels. From our background research it seemed that Whatman 41 was the most favorable. Therefore,

Table 8. Impurity Levels in the Ammonium Citrate Buffer Blank

run	Metal Concentration (ppb)			
	Cu	Pb	Cd	Zn
1	0.23	0.63	0.12	1.48
2	0.83	0.34	0.45	0.00
3	1.14	0.31	1.00	2.02
4	1.09	0.61	0.31	0.00
5	0.86	0.37	0.51	1.70
Average	$0.83 \pm .36$	$0.45 \pm .16$	$0.48 \pm .33$	$1.04 \pm .97$

the following experiments were designed to test this hypothesis.

#### Procedure

Circles, 22.40 millimeters in diameter, were cut from RAC 2292-41 (Whatman 41) filter tape with a stainless steel cork bore. The paper circles were then transferred into an acid leached Pyrex glass tube and extracted with 5.000 milliliters of the ammonium citrate buffer by means of agitation for 20 to 30 minutes. The agitation was effected either by stirring with a magnetic stirrer while bubbling vigorously nitrogen through the solution or by placing in an ultrasonic bath. At the end of the extraction time the solution was deaerated for ten minutes. Then the metals were plated at -1.3 volts into a 1 microliter mercury drop for 120 seconds while stirring and 30 more seconds quiescent. The anodic stripping was performed at a sweep rate of 5 millivolts per second with a 30 Hertz, 50 millivolts amplitude, square-wave superimposed on the ramp voltage. The sensitivity was 0.40  $\mu$  coulombs: full scale with 60 ohms positive feedback compensation and 1 second RC filter. The sample solutions were quantitated through the standard addition technique. A five minute deaeration time followed the addition of a metal spiking solution.

#### Results

The results of twelve determinations of the concentration of copper, lead, cadmium, and zinc in a 22.40 millimeter diameter Whatman 41 filter circle are shown in Table 9. By comparison to Table 8 it can be seen that the contribution of the filter to the total blank impurity level is about the same as the buffer for copper and cadmium while slightly higher in terms of the lead. Zinc, on the other hand,

Table 9. Impurity Levels in the Whatman 41 Filter Blank.

RUN	Metal Concentration (ppb)			
	Cu	Pb	Cd	Zn
1	0.05	1.15	0.00	0.46
2	0.46	2.16	0.40	5.07
3	1.35	1.71	0.01	11.25
4	1.77	1.20	0.93	0.98
5	0.87	1.64	0.61	7.57
6	2.29	2.35	0.00	11.30
7	1.41	1.20	1.05	12.05
8	0.66	1.58	0.34	7.48
9	1.60	1.91	0.01	4.51
10	2.51	1.88	0.89	11.76
11	0.84	1.30	0.39	4.51
12	1.61	1.59	0.10	8.63
Average	1.29 $\pm$ .73	1.69 $\pm$ .37	0.39 $\pm$ .39	7.13 $\pm$ 4.37

seems to come in relatively large and variable amounts from the filter which makes the determination less reliable at this low level.

#### Efficiency of the Ultrasonic Acid Extraction

From the work of Jernigan, Ray and Duce [65] and from that of Janssens and Dams [66] on the ultrasonic acid extraction of lead from particulate matter filter samples one is bound to conclude that this digestion technique is certainly worthwhile exploring further. As was reported previously, Jernigan et al, obtained a 98 percent extraction efficiency for lead in particulate matter after eluting the sample with 0.1M  $\text{HNO}_3$  in an ultrasonic cleaner. Janssens and Dams confirmed that indeed, 0.1M  $\text{HNO}_3$  was the most efficient acid concentration for the extraction, and proved that there was no statistical difference between the results obtained from duplicate samples digested ultrasonically or by the low-temperature ashing technique.

This set of experiments were designed to confirm the advantages of the combined acid - ultrasonic extraction and to compare the results to a buffer- ultrasonic extraction.

Procedure. Circles 22.40 mm in diameter of Whatman 41 were washed with 0.1M  $\text{HNO}_3$ , rinsed with reagent-grade water and dried in an oven for 15 minutes at  $75^\circ\text{C}$ . Each filter circle was spiked with 25  $\mu\text{l}$  of a standard solution containing 10 ppm of Cu, Pb, Cd, and Zn, then dried for five minutes at  $75^\circ\text{C}$ .

A spiked filter was transferred into each of several acid leached Pyrex glass tubes and five milliliters of either 0.1M Ultrex  $\text{HNO}_3$  or 0.2M ammonium citrate pH 3 buffer were added. These test solutions were

then placed in an ultrasonic cleaner for 15 minutes. After this time the solutions with buffer were directly analyzed as described in the previous section, while the acid extracts were neutralized with 100  $\mu$ l of concentrated Ultrex  $\text{NH}_4\text{OH}$  followed by the addition of 5.000 ml of buffer, before analysis.

Results. A summary of the results of this experiment is presented in Table 10. In comparing the acid and the buffer ultrasonic extraction one must remember that the maximum metal concentration for the acid extraction is half (25 ppb) that of the buffer extraction (50 ppb) since the volume of the acid extract was doubled by the addition of five milliliters of buffer after neutralization. It is of interest to notice that the buffer extraction seems not be as efficient as the acid extraction. One would expect that since the buffer extracts have twice the metal concentration of the acid extracts, their standard deviation should be comparatively smaller, e.g., the larger the amount of material to be determined, the less susceptible the results should be to random variations in the blank, etc. Since the impurity level of the blank was of 1 ppb or less for three of the metals, the buffer extracts were 50 times the blank value, while the acid extracts were only 25 times. In addition, although the extraction of copper and lead by the buffer seems adequate, the extraction of cadmium and zinc is too low. For this reason, the general procedure for the analysis of the concentration of copper, lead, cadmium, and zinc in particulate matter made use of a 0.1M  $\text{HNO}_3$  extraction, combined with the ultrasonic agitation, followed by neutralization with Ultrex



Table 10. Ultrasonic Extraction Efficiency:  
Buffer Versus Nitric Acid.

Eluting Reagent	Metals (ppb)			
	Copper	Lead	Cadmium	Zinc
0.1N HNO <sub>3</sub> (3 determinations)	20.9 ± 3.47	23.8 ± 1.18	21.3 ± 1.18	26.9 ± 4.55
Buffer (5 determinations)	50.0 ± 5.25	45.8 ± 7.61	36.0 ± 6.43	39.0 ± 7.26

$\text{NH}_4\text{OH}$  and final dilution to ten milliliters with 0.2M ammonium citrate pH 3 buffer.

#### Interference Studies

Previous studies of the ammonium citrate buffer system indicate that Ni(II), Co(II), Mn(II), Cr(III), Cr(VI) and Al(III) do not interfere in the polarographic analysis of copper, lead, cadmium and zinc because no reduction wave is obtained at pH 3 [99]. Sn(II) ( $E_{\frac{1}{2}} = -0.21$  volts) and Sb(III) ( $E_{\frac{1}{2}} = -0.64$ ) could interfere with the determination of copper and cadmium, respectively, but since the sensitivity for these metal is much lower than for Cd and Cu (which are preconcentrated by electrodeposition) and since their concentration in air is extremely low, tin and antimony should not cause any interference in this analysis. However, should these metals be in high concentrations, say above 1 ppm, their interference could be eliminated by adding 0.5 milliliters of Ultrex  $\text{HNO}_3$  to the acid - ultrasonic extract and evaporating to dryness to oxidize the metals to the higher, electro-inactive oxidation state. A similar procedure should be employed should vanadium and arsenic be present in similar amounts. No interference of 1 ppm of As(III) or V(V) with 25 ppb of Cu, Pb, Cd, and Zn was found in this study.

Selenium interferes by forming a film on the hanging mercury drop electrode. The interference appears as a shoulder on the lead stripping peak and causes the copper stripping peak to be non-gaussian. Taylor [99] uses ascorbic acid to reduce the selenium (IV) to selenium metal and eliminate the interference.

### Iron (III) Interference

The most potentially dangerous interference to this method is iron (III). It is certainly one of the common components of the metal aerosol and its concentrations, after all sample preparation steps, can exceed 300 ppb. Chau et al. [100] reported that Fe(III) interferes at the 25 ppb level by suppressing the peaks of Cu, Pb, Cd, and Zn while Taylor [99] attributes the interference to its oxidizing action on the metals in the amalgam, when present at levels greater than the metals of interest. In our study the interference of iron (III) at the 100 ppb level was observed in the form of a shoulder on a 25 ppb copper peak. At the 400 ppb level of Fe(III) it was impossible to determine 25 ppb of Cu (II) under the conditions of the experiment. Traditionally, the iron(III) interference has been controlled with hydroxylamine hydrochloride (HAH) [101,102]. Ferric ions are reduced to ferrous ions by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  such that 280 ppb of Fe(III) can be tolerated in the presence of HAH [100]. Our attempts to use this method failed because the high concentration of chloride introduced by HAH complexes the mercury, shifting its wave toward the more negative voltage region. The copper peak then appears as a shoulder to the bigger mercury dissolution wave. Other attempts to control the interference of Fe(III) which were studied include the variation of plating time and the use of complexing agents. These are described below.

Variation of Plating Time. Since the anodic stripping analysis technique cannot be employed for the determination of metals that do not form a mercury amalgam, e.g., iron, this apparent disadvantage can be profitably used to increase the signal of the metal of interest to

a point where the interfering signal of the metal is no longer significant. This is achieved by increasing the plating time and therefore the concentration of the metal in the amalgam. Satisfactory results were obtained at the 100 ppb level of Fe(III) versus 25 ppb of copper when the plating time was doubled from 120 seconds to 240 seconds. The nearly two-fold increase in the copper peak height projected well above the iron interference. Longer plating times may be appropriate with a higher iron to copper ratio.

Use of Complexing Agents. Numerous complexing agents are commonly used for the photometric determination or masking of iron(III). Nevertheless, applications to polarographic analysis are extremely scarce. In this work, preliminary test of the effect of fluoride, phosphate and sulfosalicylic acid (SSA) on the iron (III) reduction wave were performed. These consisted of adding a few mgs of the chelating agents to a solution containing 10 ppm of Fe(III) in 0.2M ammonium citrate buffer and determining by polarographic forward scan with the HDME whether this addition decreased the height of the iron peak. Since preliminary results indicated that only sulfosalicylic acid affected the iron reduction wave further studies were pursued only with this reagent.

The next test performed consisted on determining if SSA would also affect the copper wave. For this purpose a solution containing 10 ppm of Fe(III) and 300 ppb of Cu(II) in pH3 buffer was analyzed by anodic stripping under the conditions previously described except that the sensitivity was  $4.0 \mu$  coulombs full scale. As shown on Figure 3-a, the iron peak appears as a shoulder to the copper peak and prevents

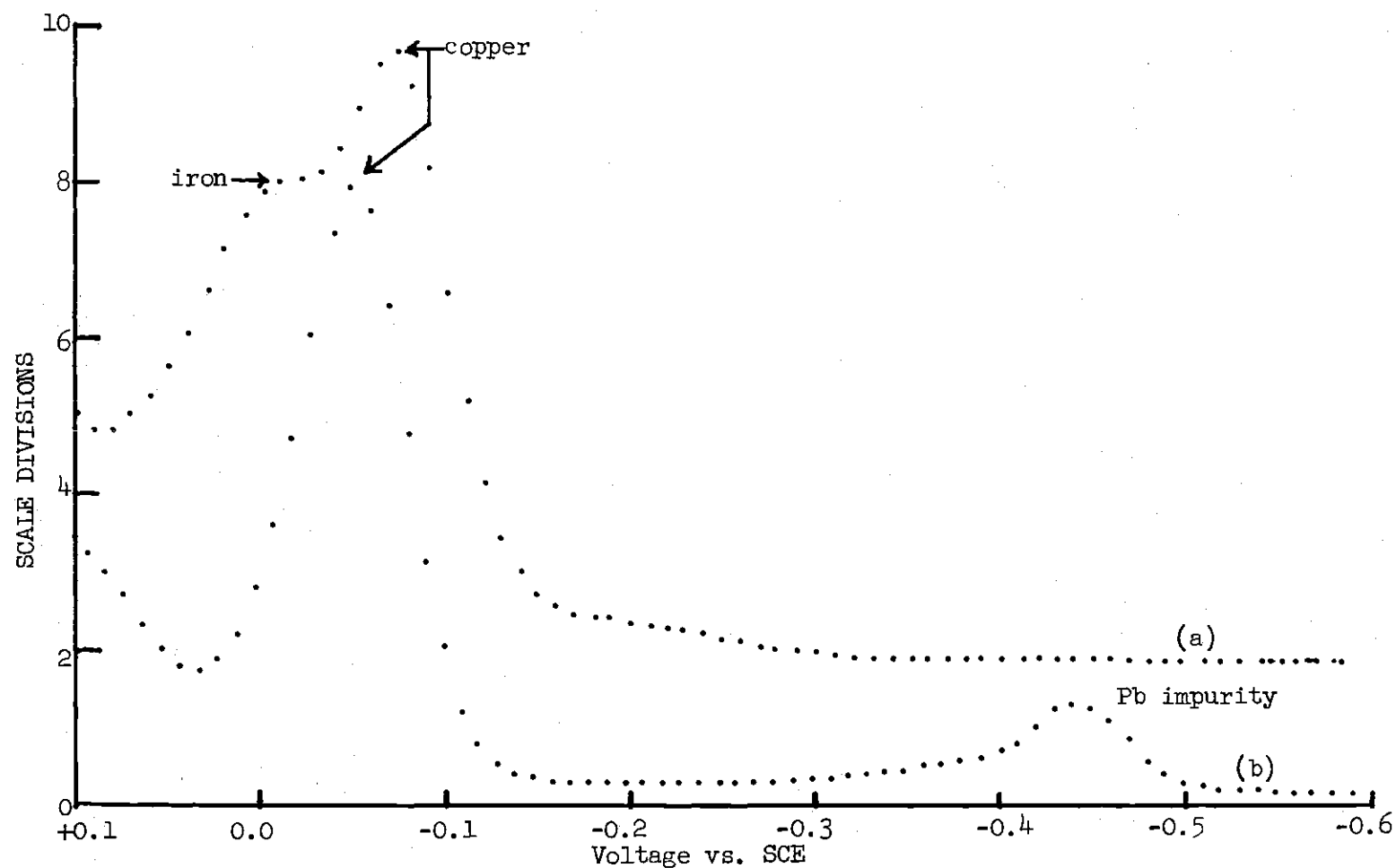


Figure 3. Effect of Sulfosalicylic Acid on the Iron (III) and Copper (II) Polarographic Wave. (a) 10 ppm Fe (III) and 300 ppb Cu (II) in 0.2 M ammonium citrate pH 3 buffer (b) same as (a) after addition of a few milligrams of sulfosalicylic acid.

securing an accurate baseline. Nevertheless upon addition of a few milligrams of SSA, the iron peak disappeared completely, while the copper peak height was unchanged (see Figure 3-b). The new small peak which appears at -0.43 volts was identified as a lead impurity from the reagent grade SSA. A similar test performed at the 660 ppb level of Fe(III) versus 166 ppb of Cu, Pd, Cd, and Zn indicated that SSA did not complex any of these metals except iron but that purification was needed in order to use SSA at the low ppb level.

Quantitative tests to determine the minimum concentration of SSA necessary to complex a given amount of iron(III) followed. These consisted of titrating (amperometrically) 10 ppm of Fe(III) in 0.2M ammonium citrate buffer versus 0.39M SSA. The results shown in Figure 4 indicate that the minimum concentration of SSA needed to complex 10 ppm of iron (II) is .07 moles per liter. However, since it would be highly improbable for an air sample obtained and analyzed through our proposed method to contain over 600 ppb of Fe(III), the results of this titration were interpolated to get a rough estimate of the amount of SSA needed for a real sample. It was estimated that a solution 0.1 percent SSA and 0.2M ammonium citrate, pH 3 should be adequate for our purposes. A solution as described above was prepared and purified by electrodeposition over a mercury pool and experiments performed with it indicated that over 1 ppm of Fe(III) could be complexed. Therefore in case of iron (III) interference 100  $\mu$ l of a ten percent solution of SSA can be used for every ten milliliters of sample to effectively eliminate the iron shoulder on the copper peak.

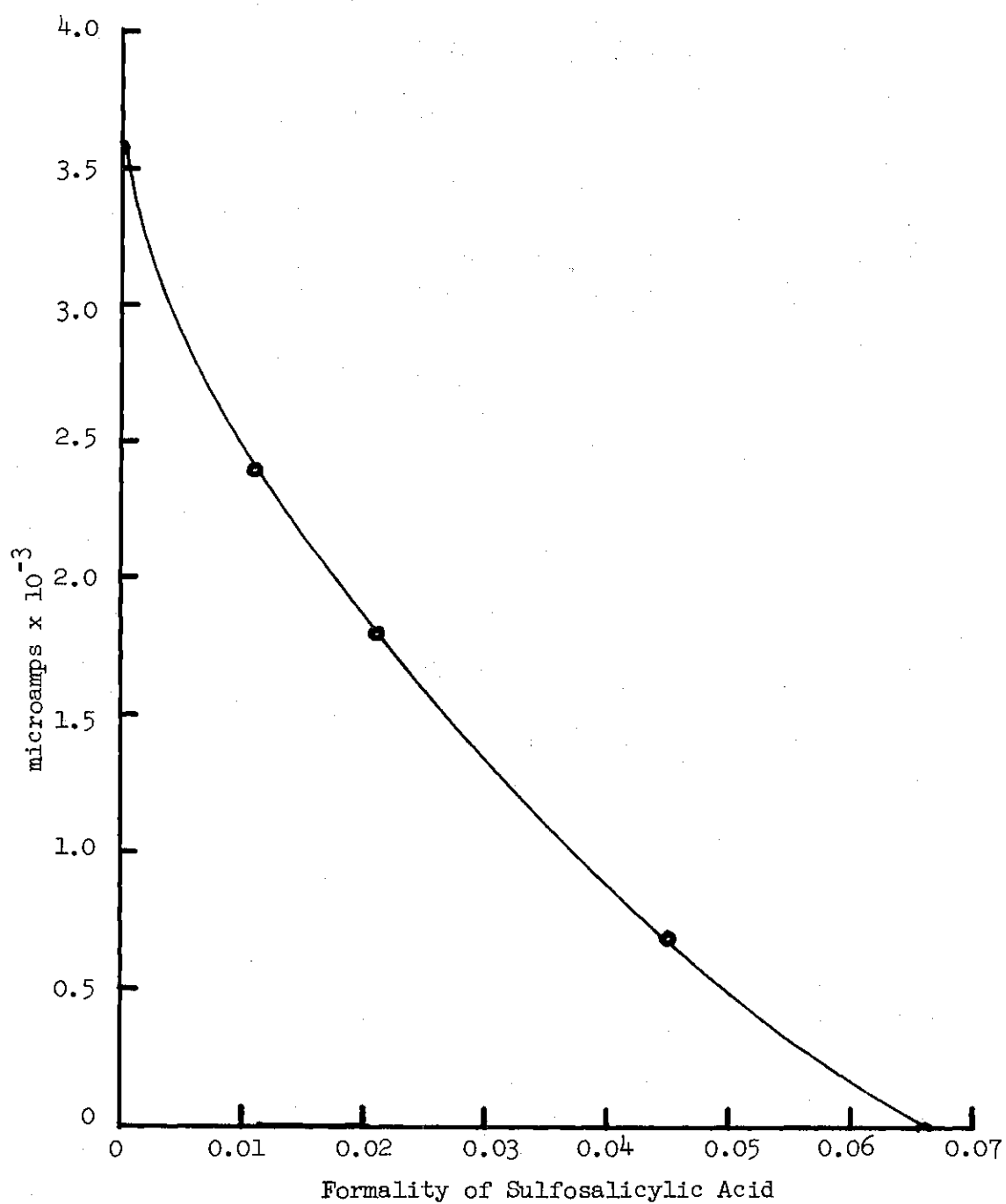


Figure 4. Amperometric Titration Curve of Iron (III) versus Sulfosalicylic Acid. Ten ppm of Fe (III) in 0.2 M ammonium citrate titrated versus 0.39M sulfosalicylic acid. (Dilution uncorrected).

### Sampling and Analysis of Whatman 41 Particulate Matter Samples

This section describes the procedure for sampling and for the simultaneous determination of copper, lead, cadmium and zinc in Whatman 41 particulate-matter samples. The results provide a measure of the three-hour variations of the airborne concentration of these metals in the immediate area surrounding the Georgia Tech campus. In addition, a comparison between variations in week days versus weekend days was obtained.

Sampling. A tape sampler was installed on top of the Fred W. Ajax Placement Center since this was the site chosen by the Division of Environmental Health Services of the Fulton County Health Department for an air monitoring station for the National Ambient Air Network. Using Whatman 41 filter tape, the sampling equipment was set to sample the ambient air at a rate of 15 cubic feet per hour (about seven liters per minute) for three hours per sample.

Sample Treatment. From each of the 25.84 millimeter diameter sample spots made on the Whatman 41 filter tape, a circle 22.40 mm diameter (75.15 percent of total area) was cut with a stainless steel bore against a Teflon backing. Each circle was then transferred to an acid-leached Pyrex tube and five milliliters of 0.1M  $\text{HNO}_3$  added. The tubes were then placed in the ultrasonic cleaner for 30 minutes. After this time the samples were just neutralized with 50  $\mu\text{l}$  of Ultrex  $\text{NH}_4\text{OH}$  and adjusted to pH 3 by addition of 5.000 ml of 0.2M ammonium citrate buffer.

Analysis. The treated sample was deaerated for ten minutes



with an oxygen-free stream of nitrogen. After deaeration was completed, a one microliter mercury droplet was extruded with the HDME. The magnetic stirrer was then turned on, adjusting the stirring rate such that the solution beneath the mercury was well stirred, but there was no visible movement of the mercury droplet. Once the stirring rate was set, it was kept constant throughout the day.

The metals were then electrodeposited at -1.3 volts versus the saturated calomel electrode for exactly two minutes. The magnetic stirrer was then turned off and the scan initiated exactly 30 seconds later. This quiescent period between plating and scan allowed convection to cease.

After the square-wave anodic stripping curve was run on the sample solution, the anodic stripping curve was quantitated using the standard addition technique. An appropriate aliquot of the combined copper, lead, cadmium, and zinc spiking solution was added to the sample in the polarographic cell. The solution was then deaerated for five minutes to remove the oxygen added with the spike, followed by a repeat of the electrodeposition step and scan.

Instrumental Parameters. The instrumental settings, which apply specifically to the square wave polarograph model 6-71 as described by Sturrock and Carter [92,97], are summarized in Table 11.

### Results and Discussion

Table 12 contains the results of the analysis of copper, lead, cadmium and zinc in the campus environment from Monday, July 12 to Wednesday, July 14, 1976. This data is also shown in the form of a plot of the three-hour average metal concentrations as a function of

Table 11. Instrumental Parameters for the Square-Wave Polarograph.

Initial potential	-1.3 volts	Cell current	1 ma/volt
Scan rate	5 mv/sec	gain	5
Scan direction	"+"	Square wave: frequency amplitude direction	30 Hz 25 mv "-"
Compensation	85 ohms	Deposition time	2 min/stir + 30 sec quiescent
RC filter	1 sec		
Booster	"in"	HDME drop	1 $\mu$ l

Table 12. Concentrations of Cu, Pb, Cd, and Zn in Whatman 41 Particulate Matter Samples from July 12, 1976 to July 14, 1976.

<u>Sample</u>	<u>Date</u>	<u>Time</u>	<u>Metal concentration (ng/m<sup>3</sup>)</u>			
			<u>Cu</u>	<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
1	7/12	16-19	48.9	612.6	41.6	220.9
2	7/12	19-22	25.3	862.6	23.8	39.8
3	7/12	22-1	110.1	789.3	39.6	138.1
4	7/13	1-4	98.7	8.2	0.9	23.3
5	7/13	4-7	26.9	301.1	8.5	31.7
6	7/13	7-10	32.5	428.0	10.0	66.2
7	7/13	10-13	60.8	262.0	1.1	371.9
8	7/13	13-16	19.7	156.7	2.4	63.7
9	7/13	16-19	15.6	217.0	0.9	0.0
10	7/13	19-22	11.9	336.0	0.8	45.8
11	7/13	22-1	25.4	650.0	4.5	0.0
12	7/14	1-4	12.1	275.1	2.8	4.2

time in Figure 5. It is interesting to notice that at first glance the concentration pattern seems to be the same for all four metals. For instance, there are three maxima: one on Monday evening, a second one mid-day on Tuesday, and the third one on Tuesday evening. This factor alone would suggest that the metals have a common source. Nevertheless, closer examination of Figure 5 shows that the maxima are slightly displaced and not exactly coincident. The lead pattern (Figure 5-c) can be easily related to traffic, which is the major source of this metal: As the afternoon approaches and early evening traffic builds up, the incoming solar radiation decreases, changing the atmospheric temperature profile to establish an inversion. Under these conditions, the air masses cannot be dispersed effectively, resulting in the accumulation of automobile exhaust, which, in turn, causes high lead concentrations, mainly in the form of lead bromide. A similar situation occurs in the early morning, resulting in the build-up of the lead concentration before noon. Of the other three metals, only cadmium seems to follow closely the lead pattern. This suggests that, while traffic may be a contributing factor to the concentration of all four metals, there may be independent sources to the airborne concentration of copper and zinc.

On the other hand, the results obtained for the analysis of samples taken from Saturday, July 17 to Monday, July 19, 1977 show a completely different pattern for almost each one of the metals. These are shown in Figure 6 and Table 13. As can be deduced from the plot of the data, it is doubtful that one could blame traffic for the

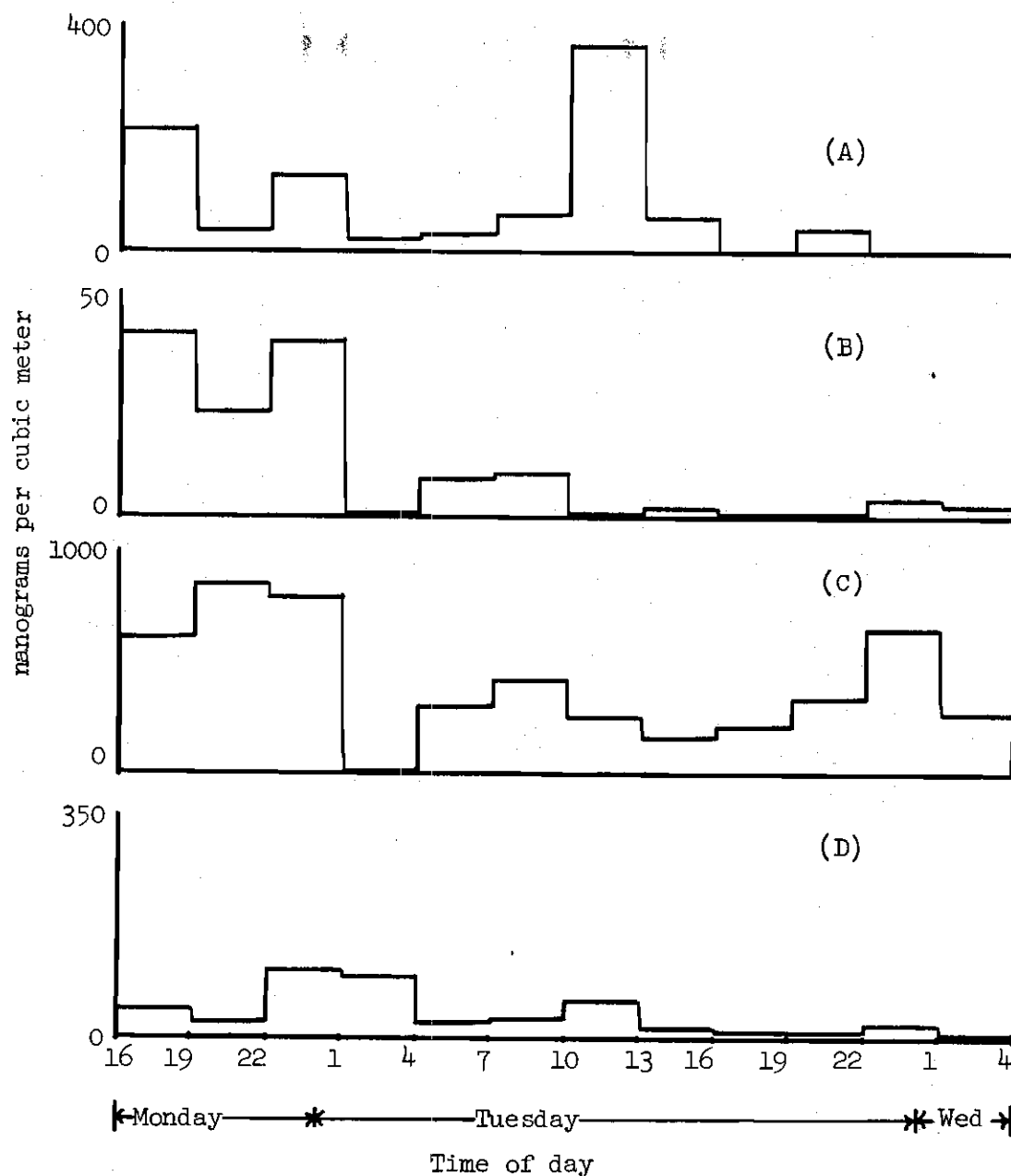


Figure 5. Time Variations in the Airborne Concentration of (A) Zinc, (b) Cadmium, (C) Lead, (D) Copper for the Time Period of July 12, 1976 to July 14, 1976. Three-hour Average Samples on Whatman 41 Filter Paper. Notice that while the time scale in the same, the concentration scale varies for each metal.

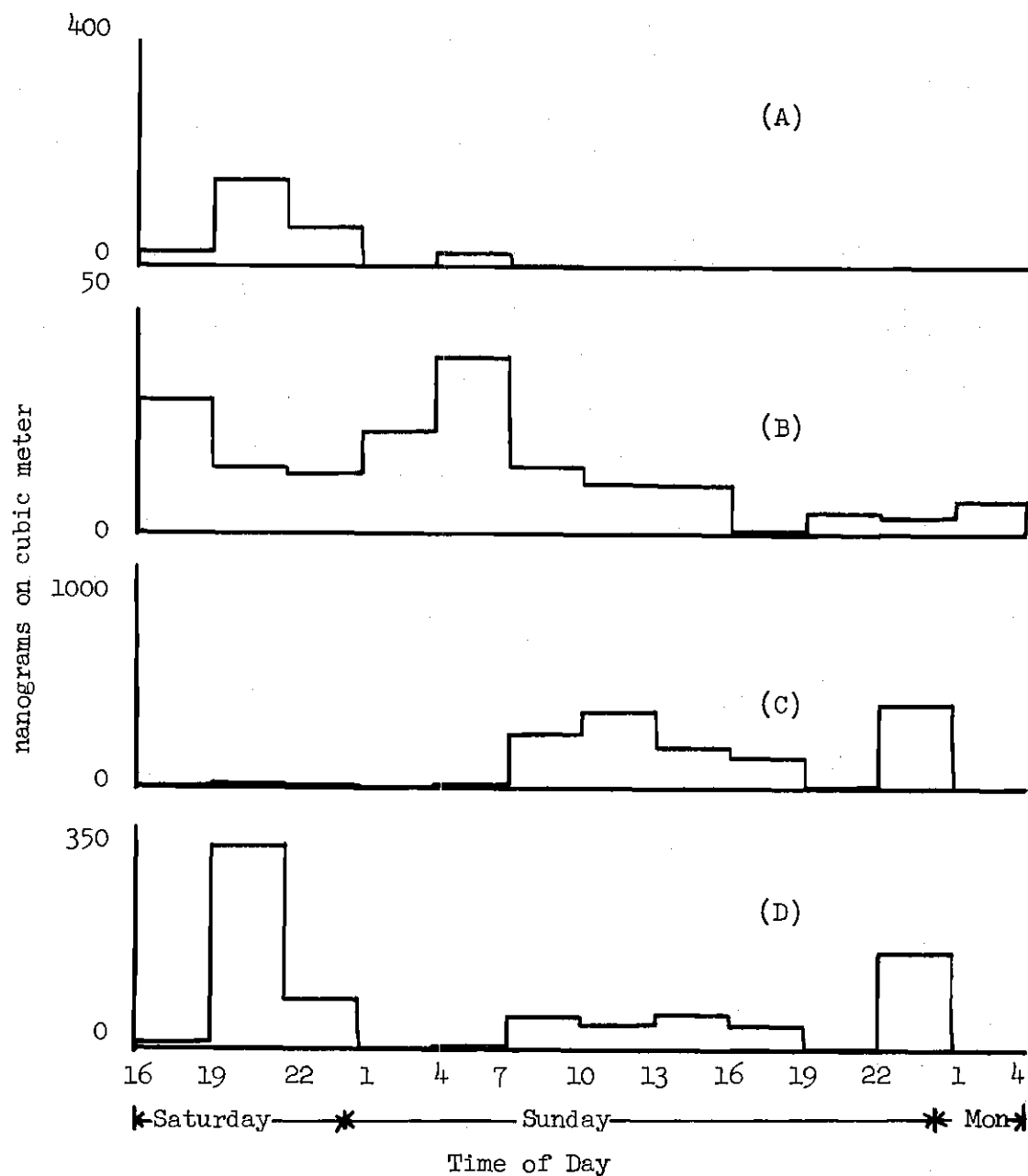


Figure 6. Time Variations in the Airborne Concentrations of (A) Zinc, (B) Cadmium, (C) Lead and (D) Copper for the time period of July 17, 1976 to July 19, 1976. Three-hour average samples on Whatman 41 filter paper. Notice that while the time scale is the same, the concentration scale each metal.

Table 13. Concentration of Cu, Pb, Cd, and Zn in Whatman 41 Particulate Matter Samples from July 17, 1976 to July 19, 1976.

<u>Sample</u>	<u>Date</u>	<u>Time</u>	<u>Metal concentration (ng/m<sup>3</sup>)</u>			
			<u>Cu</u>	<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
1	7/17	16-19	11.9	14.1	30.8	28.1
2	7/17	19-22	321.7	27.8	15.3	158.2
3	7/17	22-1	80.6	20.6	13.6	74.5
4	7/18	1-4	0.0	0.0	23.1	0.0
5	7/18	4-7	7.5	19.8	40.1	28.8
6	7/18	7-10	56.3	243.8	15.6	7.7
7	7/18	10-13	39.0	350.7	12.0	0.0
8	7/18	13-16	58.3	194.0	11.0	0.0
9	7/18	16-19	40.0	142.8	1.0	0.0
10	7/18	19-22	0.0	10.2	5.3	0.0
11	7/18	22-1	155.2	389.8	3.8	0.0
12	7/19	1-4	2.0	0.0	8.1	0.0

relatively large concentrations of Cu, Cd, and Zn since these predominate even when the lead concentration is minimum. The zinc concentration in the campus environment goes to undetectable levels at a time when the lead concentration starts increasing. The cadmium level shows a completely independent pattern with a maximum average concentration around dawn on Sunday. Only copper has high levels when lead does, but not even the concentration of this metal can be entirely correlated to the lead pattern. What the data suggests is the presence of either, an independent metal sources in the area with different work patterns or of one large source that performs operations with different metals, in addition to the traffic source.

A better comparison of the variation in the concentration pattern of the copper, lead, cadmium, and zinc between week days and weekend can be obtained through examination of Figures 7 to 10. In Figure 7 the variation in the concentration of zinc is shown. The fact that there is a steady pattern during weekdays but an interrupted pattern during the weekend seems to suggest a source that ceases operations on Sunday. On the other hand, the patterns of cadmium and copper (Figures 8 and 10, respectively) do not change, although concentrations are somewhat higher during the weekend. These two patterns suggest a source that works continuously, seven days a week. The lead concentration pattern (Figure 9) can be attributed mainly to traffic as the concentrations are lower at the times of less traffic flow.

#### Filter Comparison

This set of experiments were designed to compare the impurity



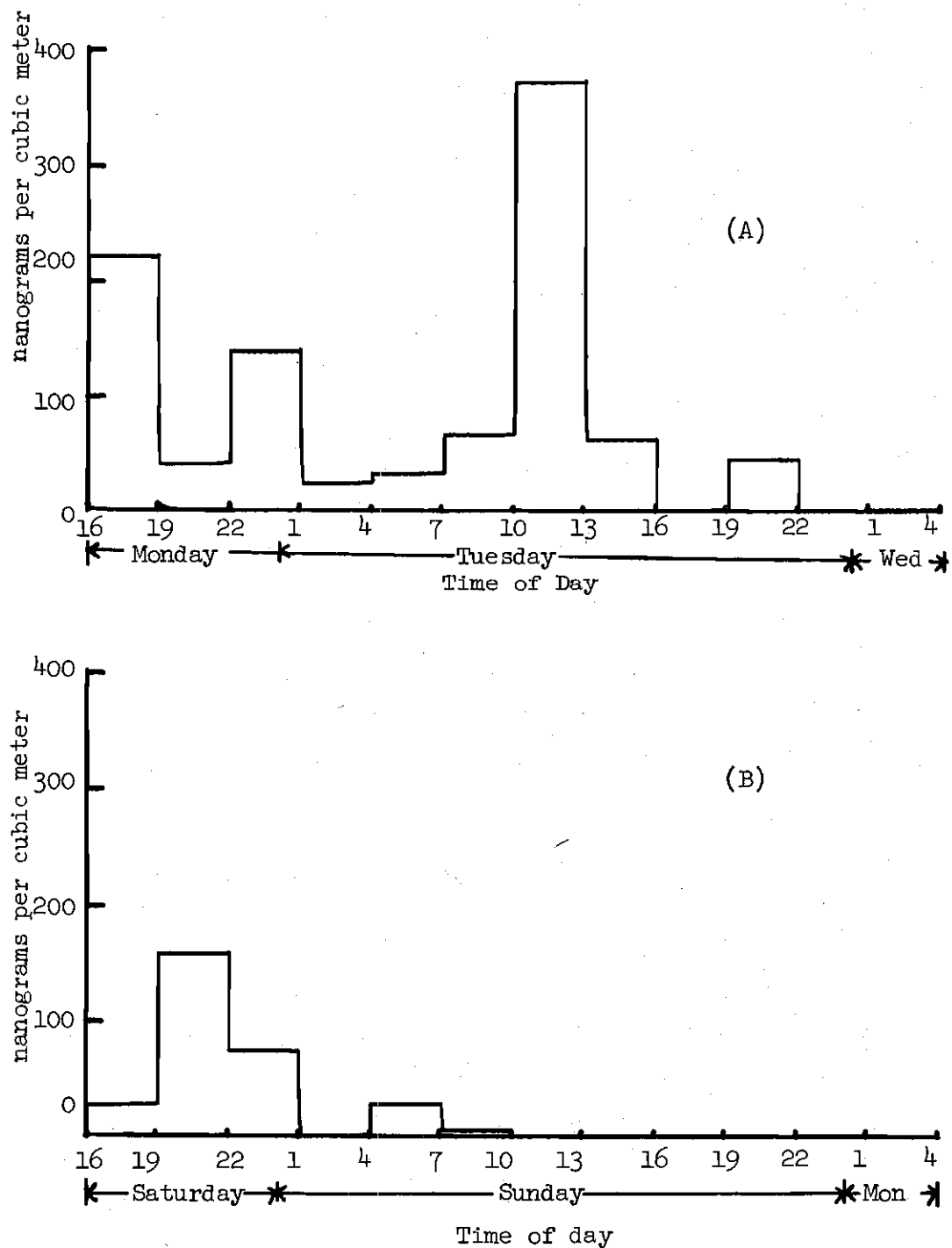


Figure 7. Time Variations in the Airborne Zinc Concentration. Weekday versus weekend samples. Three-hour average samples for the time period of (A) July 12, 1976 to July 14, 1976, (B) July 17, 1976 to July 19, 1976.

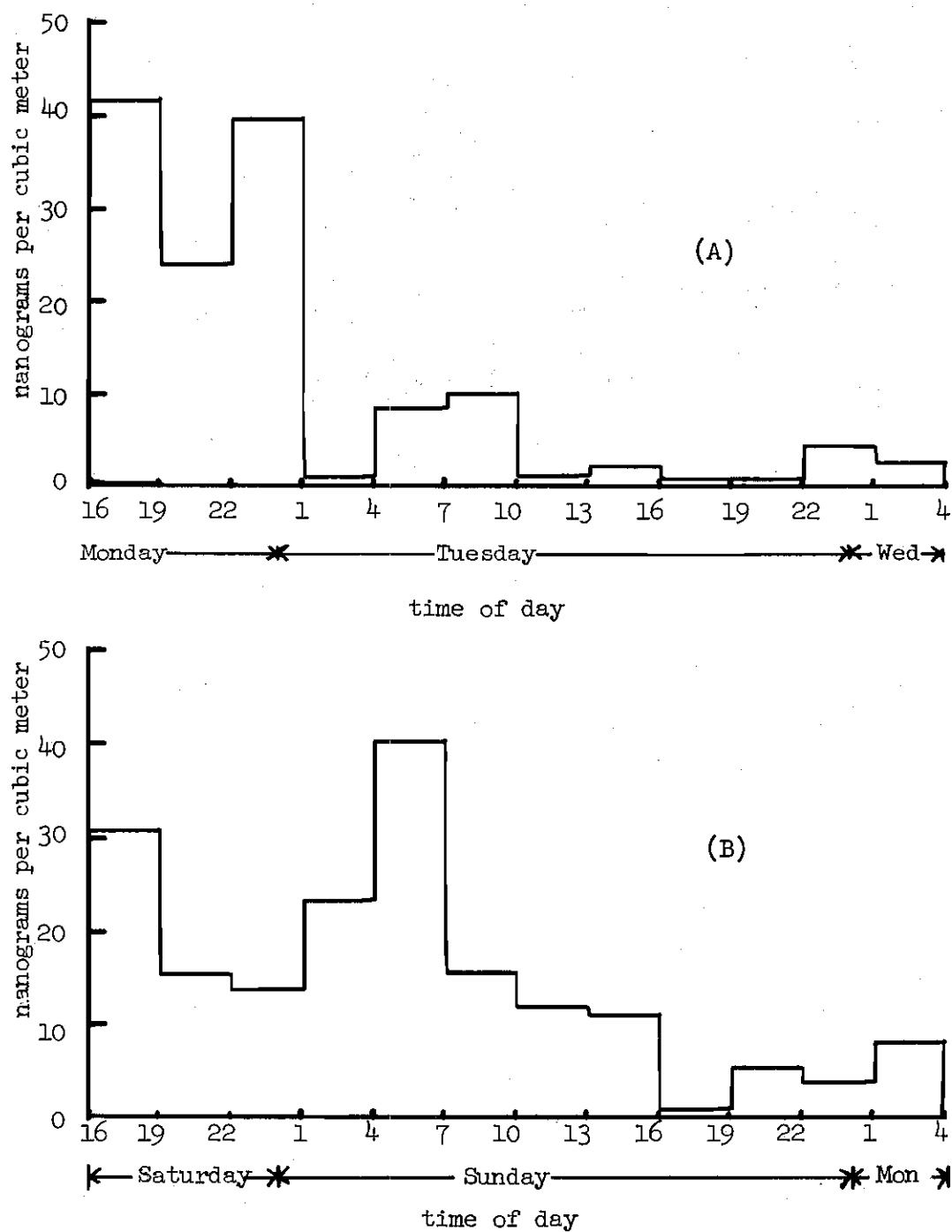


Figure 8. Time Variation in the Airborne Cadmium Concentration: Week day versus weekend samples. Three-hour average samples for the time period of (A) July 12, 1976 to July 14, 1976, (B) July 17, 1976 to July 19, 1976.

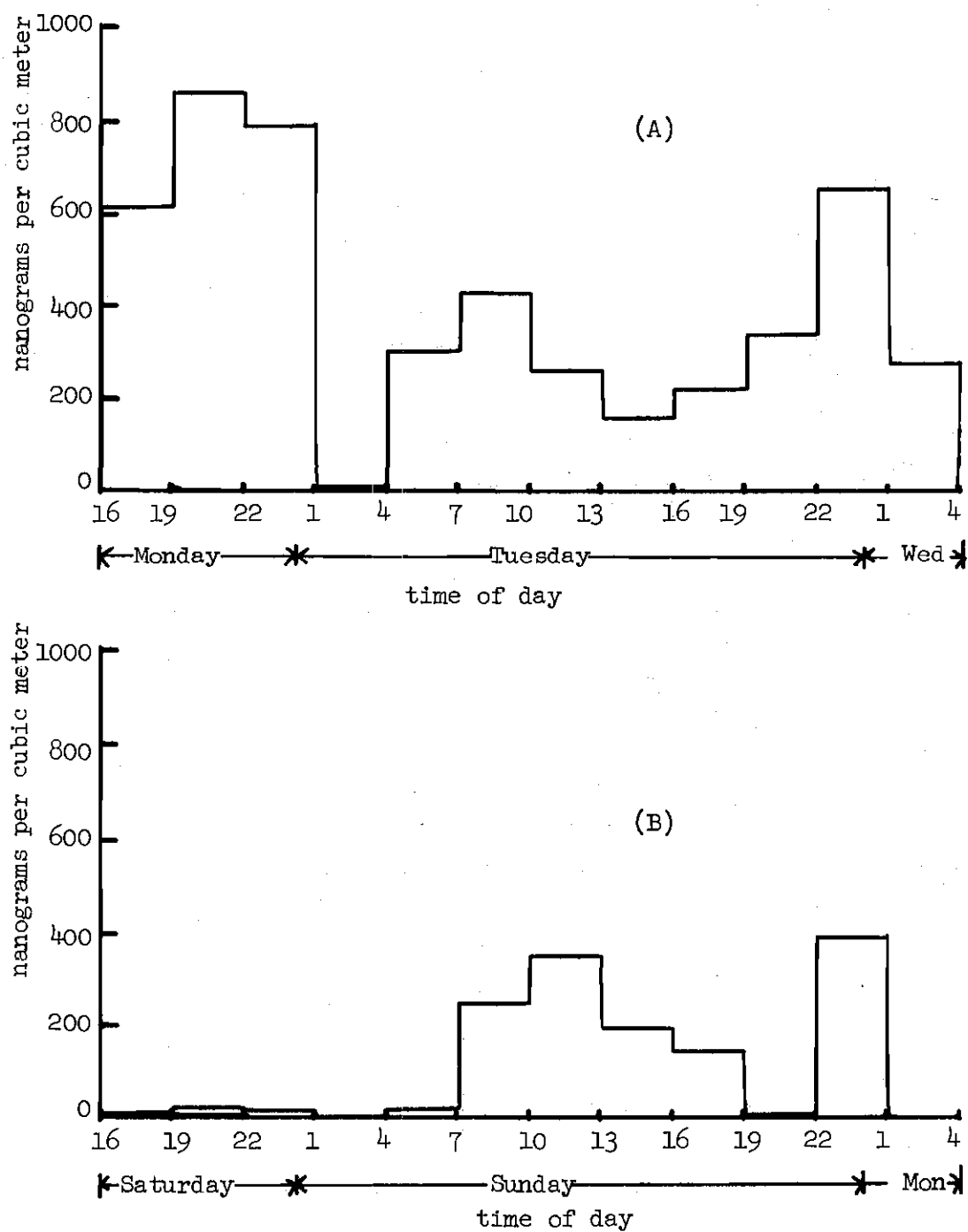


Figure 9. Time Variations in the Airborne Lead Concentrations: Weekday versus weekend samples. Three-hour average samples for the time period of A) July 12, 1976 to July 14, 1976, B) July 17, 1976 to July 19, 1976.

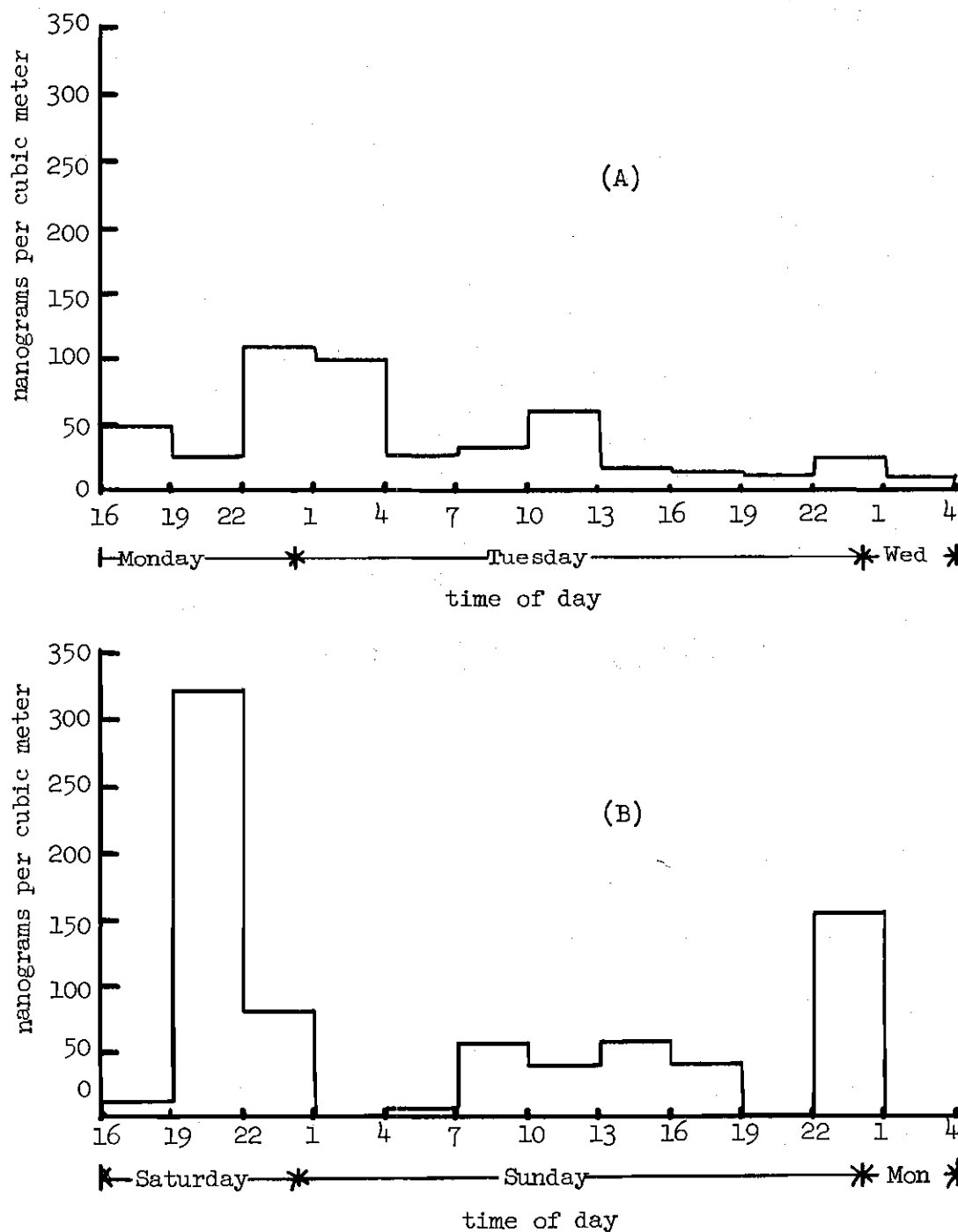


Figure 10. Time Variation in the Airborne Copper Concentration: Weekday versus weekend samples. Three-hour average samples for the time period of (A) July 12, 1976 to July 14, 1976, (B) July 17, 1976 to July 19, 1976.

levels and sampling characteristics of Whatman 41 with Whatman 540, 541 and 542. The five-hundred series of the Whatman cellulose filters are the hardened ashless grade filters. These are filter papers made from acid treated high-purity alpha cellulose (as the Whatman 41) which are hardened by treatment with strong mineral acids after manufacture. The acid treatment also results in removal of most of the trace metals and for that reason these filters should contribute very little to the impurity levels of copper, lead, cadmium, and zinc in the total blank. In addition, Whatman 540 and 542 have a higher efficiency than Whatman 41 for the retention of smaller particles [33]. This factor should be advantageous in obtaining a representative sample of the metal aerosol.

Hardened Ashless Grade Filter Blanks. The procedure outlined in the previous section for the determination of Cu, Pb, Cd, and Zn in air samples was followed with unused Whatman 540, 541, and 542 filter paper circles 22.40 mm diameter. The results are shown in Table 14. As can be seen, these filters are extremely pure in relation to the metals sought since the data presented corresponds to the total combined blank (that is, reagents and filter impurity levels), not to the filter contribution alone (compare with Table 9 for the Whatman 41 blank). Highly significant is the fact that the amount of zinc has been drastically reduced to maximum of 1.4 ppb or only 0.4 ppb above the buffer level (See Table 8).

Sampling Efficiency. In order to compare the sampling efficiency of Whatman 41 against the hardened ashless-grade series the arrangement shown in Figure 11a was used. To obtain two simultaneous

Table 14. Impurity Levels in the Whatman Hardened Ashless Filters.  
The Concentrations Shown here are for the Total Filter  
and Reagent Blank after Ultrasonic Digestion.

<u>Sample</u>	<u>Filter</u>	Metal concentration (ppb)			
		<u>Cu</u>	<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
1	W540	1.4	0.7	0.2	1.4
2	W542	1.9	1.1	0.2	1.4
3	W541	1.1	0.01	0	0

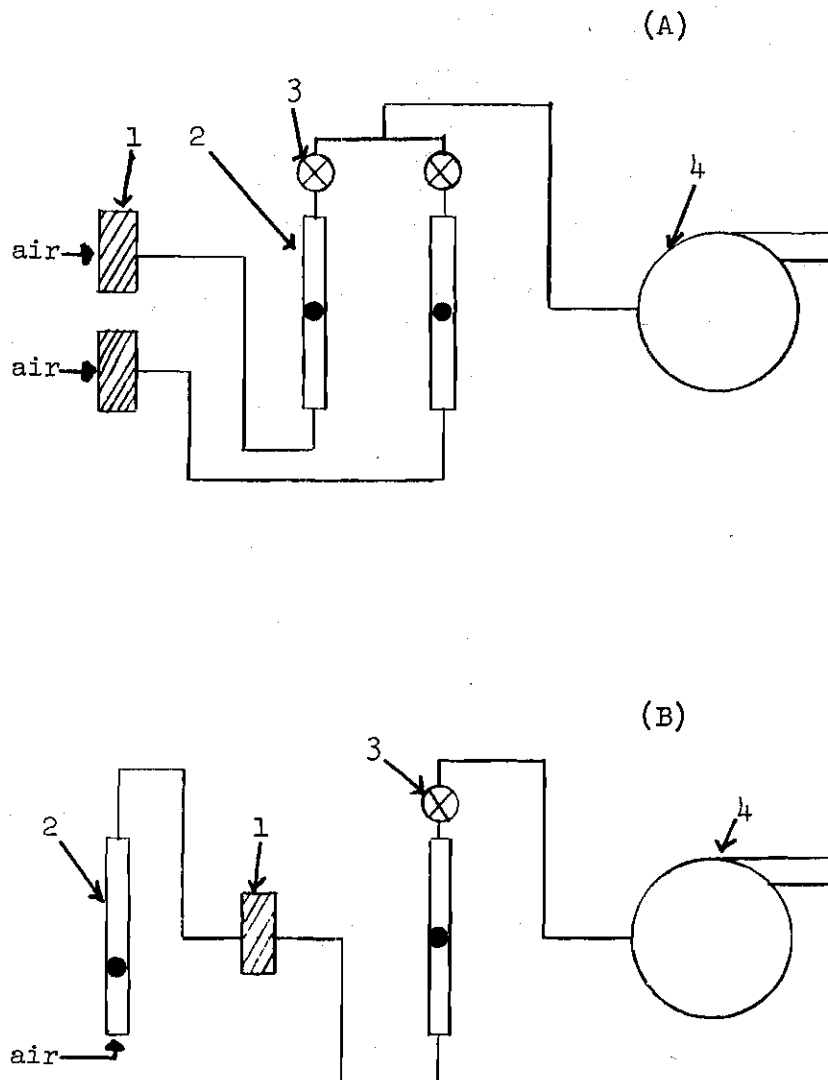


Figure 11. Air Sampling Diagrams for the Filter Comparison Experiments:

- (A) schematic for obtaining two simultaneous samples,  
 (B) schematic for flowrate connection due to pressure shop.  
 Symbols: (1) filter and filter holder assembly,  
 (2) flowmeter, (3) flowrate regulating valve,  
 (4) vacuum pump.

samples. The filter holders, made of two modified fritted disc funnels (Fisher Scientific Company 10-358F), were attached to calibrated flowmeters (Matheson 605) fitted with a flow regulating valve. The valves were used to adjust the air flowrate such that the same reading would be obtained from the flowmeters. However, since there is a higher pressure drop, and consequently a lower flowrate, through Whatman 540 and 542 when compared with Whatman 41 due to the smaller interfiber distance in these hardened ashless filters, the arrangement shown in Figure 11b was used to obtain the pressure drop-corrected flowrate. Simultaneous samples of Whatman 41 and the filter of interest collected for one hour at an average rate of 13 liters per minute were analyzed using the procedure previously outlined.

Results of these experiments are shown in Table 15. In examining the results it must be borne in mind that one part per billion of the metal in the polarographic cell is roughly equivalent to fifteen nanograms per cubic meter of the metal in air so that small differences in the metal concentrations tend have a bigger spread upon conversion to mass/volume units. Additionally, it must also be considered that Whatman 41 has a higher variability than the hardened-grade filter in the metal concentration in the blank such that this factor will have an effect in the results. These experiments show that there is little difference between Whatman 41 and 541 as expected since these two filters have the same interfiber distance. The higher amount of cadmium from the Whatman 541 may be attributed to a more efficient removal from the filter surface, while the lower copper concentration may be traced to a higher Whatman 41 copper blank. The results for



Table 15. Sampling Efficiency of Whatman 41 Versus Whatman 540, 541 and 542.

<u>Test</u>	<u>Filter</u>	<u>Metal concentration (ng/m<sup>3</sup>)</u>			
		<u>Cu</u>	<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
1	W41	17.2	690.7	16.7	66.4
	W541	2.9	632.5	58.6	41.2
2	W41	0.0	399.6	70.1	0.0
	W540	16.7	277.0	112.3	140.2
3	W41	0.0	394.7	28.4	0.0
	W542	24.9	331.8	20.9	95.7

the Whatman 41 versus 540 indicate that a better efficiency for the sampling of copper, cadmium and zinc may be obtained with Whatman 540. These results seem to be confirmed by the comparison of Whatman 41 to 542, specially in relation to the concentration of copper and zinc. Since the Whatman 540 and 542 have approximately one-third and one-eighth the interfiber distance of the Whatman 41 it seems logical to conclude that the entrapment of smaller particle through direct interception the former filters achieve, is responsible for the higher concentrations of copper, cadmium and zinc and that therefore, these are better filters than Whatman 41 for sampling the metal aerosol.

#### Sampling and Analyses of Whatman 542 Particulate Matter Samples.

This section describes the procedure used to sample particulate matter with the Whatman 542 filter. Since this filter is not commercially available in rolls that fit the tape sampler previously described, a Whatman 542 filter tape was obtained by stapling together 11" x 1 $\frac{1}{2}$ " strips and punching guiding sprockets every one and a half inches. After installation of the filter tape in the tape sampler it was noticed that the higher pressure drop through this filter caused it to collapse. To prevent this, a filter support made of a fine aluminum mesh was placed inside the air sampling head. In addition, a relay circuit which stopped the pump action in-between samples was used to allow pressure equilibration in the sampling head such that the filter tape could be advanced without tearing. One-hour average samples were then taken at a rate of 17 liters per minute from the top of the Fred W. Ajax Placement Center.

The concentrations of copper, lead, cadmium, and zinc resulting from the Whatman 542 experiments is presented in Table 16 and plotted as a function of time in Figure 12. The obvious advantage the one-hour average sample has over the three-hour one is that with the former one can zero-in better on the sometimes subtle concentration variations which occur as the day progresses. For instance, if one were to report a lead maximum for Wednesday night using the data on Table 12, the best that could be done was to report  $650 \text{ ng/m}^3$  between 22:00 and 1:00 hours of Thursday morning. On the other hand, the one-hour average samples provide more accurate information reporting a lead maximum of  $1710 \text{ ng/m}^3$  between 23:00 and 24:00 hours on Wednesday night (see Table 16). In addition, it is this kind of short-term information that can be more closely associated with meteorological changes or variations in industrial emission patterns and for that reason it is more pertinent to the identification of pollution sources, and to the prevention of health episodes. These advantages are not a direct result of the use of Whatman 542 for air sampling, as similar experiments could have been performed with the Whatman 41 filter tape. However, the hardened-ashless filter does provide the advantage of more consistent and lower background blanks. Under the sampling conditions of this experiment the metal impurity levels of Whatman 542 for the total blank as presented in Table 14 are equivalent to 24.0, 13.9, 2.5, and 17.6 nanograms per cubic meter of Cu, Lead, Cd, and Zn, respectively. This compares favorably against 26.5, 26.5, 11.3, and 103.3 nanograms per cubic meter of Cu, Pb, Cd, and Zn, respectively, for the total blank of Whatman 41 as calculated from the data in Tables 8 and 9. In addition, the 542

Table 16. Concentration of Cu, Pb, Cd and Zn in Whatman 542 Particulate Matter Samples from November 3, 1976 to November 4, 1976.

<u>Sample</u>	<u>Date</u>	<u>Time</u>	<u>Cu</u>	<u>Metal Concentrations (ng/m<sup>3</sup>)</u>		
				<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
1	11/3	17-18	67.2	1116.9	72.2	185.7
2	11/3	18-19	78.0	1197.0	4.2	120.7
3	11/3	19-20	76.7	1208.3	3.9	100.7
4	11/3	20-21	47.3	1004.6	0.0	116.4
5	11/3	21-22	0.0	1059.7	13.6	0.0
6	11/3	22-23	8.9	1232.4	20.8	86.8
7	11/3	23-24	19.9	1710.0	6.3	1.3
8	11/4	0-1	37.7	769.3	22.7	22.6
9	11/4	1-2	50.7	526.0	3.9	53.9
10	11/4	2-3	0.0	480.9	13.7	8.3
11	11/4	3-4	7.4	193.3	15.8	70.6
12	11/4	4-5	0.0	540.1	0.0	19.4
13	11/4	5-6	8.4	306.8	6.4	45.6
14	11/4	6-7	5.0	330.0	0.0	0.0
15	11/4	7-8	27.1	1034.6	2.5	18.3
16	11/4	8-9	39.2	595.7	7.6	27.1
17	11/4	9-10	13.2	337.0	0.3	0.0
18	11/4	10-11	0.0	178.4	0.0	0.0
19	11/4	11-12	8.6	166.3	2.9	20.8
20	11/4	12-13	2.9	144.8	0.0	0.0
21	11/4	13-14	30.6	199.6	2.5	0.6
22	11/4	14-15	11.1	346.6	0.0	0.0
23	11/4	15-16	50.8	269.9	5.7	48.8
24	11/4	16-17	8.1	552.4	0.0	33.9

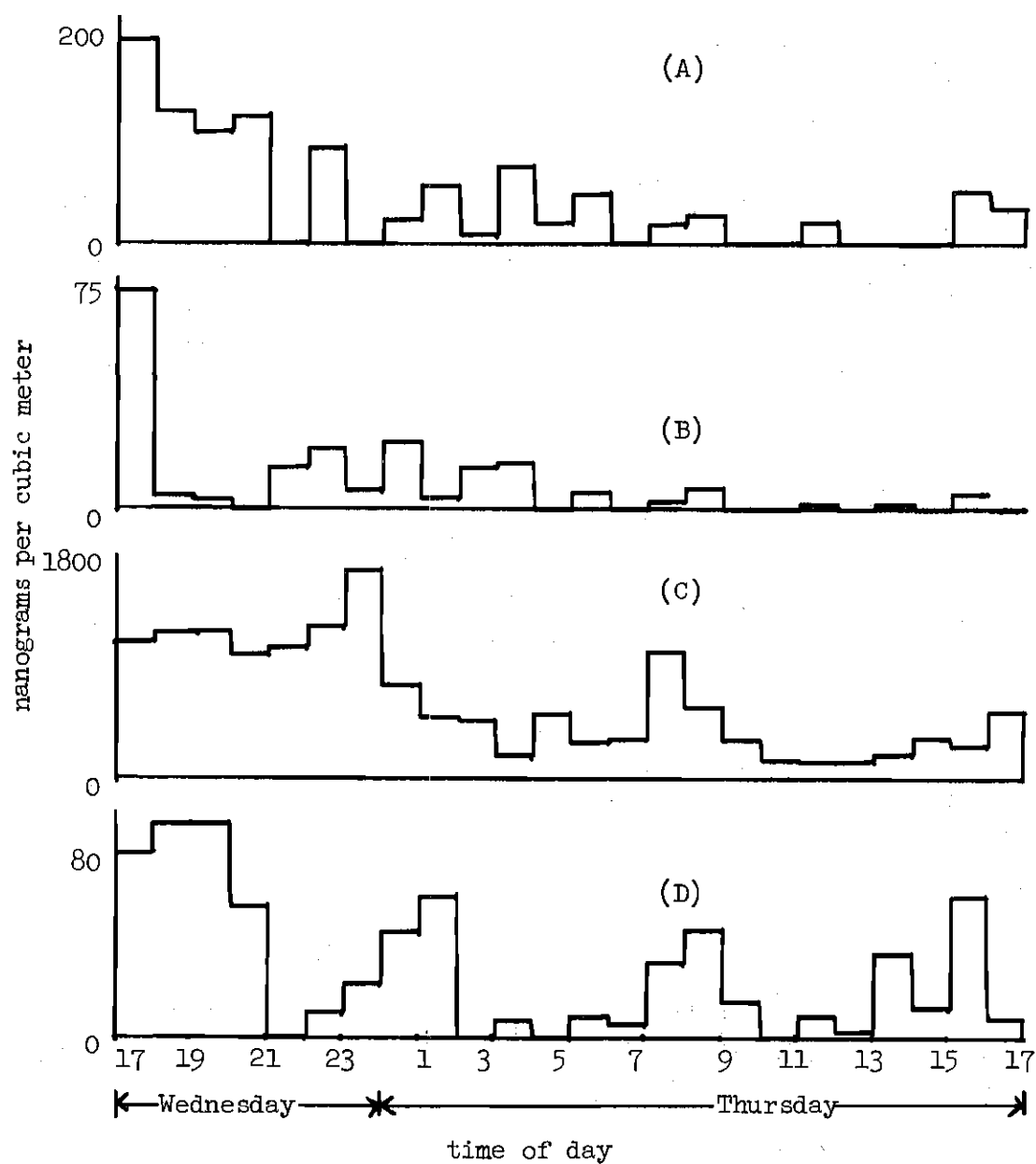


Figure 12. Time Variations in the Airborne Concentrations of (A) Zinc, (B) Cadmium, (C) Lead and (D) Copper for the time period of November 3, 1976 to November 8, 1976. One-hour average samples obtained on Whatman 542 filters. Notice that while the time scale is the same, the concentration scale varies for each metal.

filter seems to possess a higher efficiency for the collection of the particles in the microgram and submicrogram size range.

Comparison between Figures 5 and 12 indicate that the same general metal concentration pattern is consistent between three-hour average Whatman 41 samples and one-hour average Whatman 542 samples. Nevertheless, due to the difference in the sampling period, a better overall picture is obtained from the Whatman 542 particulate matter samples.

#### Miscellaneous Experiments: Alternative Digestion Method

This series of experiments was designed to examine the possibility of using a fast digestion method involving the dissolution of the Whatman 41 filter with a strong mineral acid. The hypothesis was that once the filter was dissolved, the metals would have a better opportunity to enter into solution since the contact area with the acid media would be enlarged. In addition, the strongly acidic solution would also help break-up any organic-bound metal resulting from atmospheric reactions with fuel by-products.

The effect of different concentrations of sulfuric, nitric, and hydrochloric acid on the Whatman 41 paper was studied. Only concentrated sulfuric acid seemed to dissolve the filter at room temperature to yield a clear solution with a slight yellowish tint which turned black upon warming up. In order to determine if dissolution of the filter sample with sulfuric acid could be used as a digestion step for the analysis of particulate matter samples the following tests were performed: Whatman 41 filter circles 22.40 mm in diameter which had been spiked with 25 microliters of a standard solution containing 10

ppm of Cu, Pb, Cd, and Zn, were placed in an acid-leached Pyrex glass tubes and 250  $\mu$ l of concentrated Ultrex  $H_2SO_4$  were added. After dissolution was complete, the solution was neutralized with one milliliter of concentrated Ultrex  $NH_4OH$  and adjusted to pH 3 by addition of five milliliters of 0.2M ammonium citrate buffer. A control solution containing 25  $\mu$ l of the metal spiking solution in addition to the prescribed volumes of sulfuric acid, ammonium hydroxide and ammonium citrate buffer, but without a dissolved Whatman 41 filter, was also prepared. Both of these solutions were then analyzed by square-wave anodic stripping as outlined in a previous section. Comparison between the control and the test solutions indicated that an unidentified electroactive by-product of the dissolution of the Whatman 41 filter with sulfuric acid had a half-wave potential of -1.2 volts and could possibly interfere with the determination of zinc. But more important, it was discovered that a large suppression of the peak height of Cu, Pb, Cd, and Zn occurred in the test solution containing the dissolved cellulose filter. This is probably due to metal complexation and electrochemical masking of the metal ions by products of the Whatman 41 filter dissolution. Since these two combined factors decreased the sensitivity of the method by nearly an order of magnitude, no further experiments on this alternative digestion method were performed.

#### Conclusion and Recommendations

In this study a method for the determination of the time variations of the concentration of copper, lead, cadmium and zinc in

aerosols has been presented. One-hour particulate matter samples here can be obtained with the use of a commercially-available tape sampler having a pump capable of drawing air at a rate of about 17 liters per minute. The Whatman 41 cellulose filter tape has an adequate background level for all metals sought except for zinc, whose concentrations are not only relatively high (about 7 ppb) but also quite variable. Experiments performed with the Whatman hardened ashless-grade filters indicated that improvement of the method could be achieved through the use of these filters for sampling particulate matter. These filters provide not only an extremely small contribution to the background level of copper, lead, cadmium, and zinc in the blank, but also the Whatman 540, 542 seem to increase the collection efficiency of the aerosol particles in the microgram and submicrogram range.

The application of an acid-ultrasonic agitation extraction to filter samples has been confirmed when 0.1M  $\text{HNO}_3$  is used as the eluting reagent. This technique for introducing the sample into solution is fast, convenient, efficient and specially suitable for multi-sample analysis.

The use of sulfosalicylic acid to prevent the interference of iron(III) with the determination of copper was examined. It was found that with only 0.1 percent sulfosalicylic acid, a concentration of Fe(III) as high as 1 ppm could be tolerated. This reagent provides a more convenient method to eliminate iron interference than the commonly used hydroxylamine hydrochloride since the later reagent introduces chloride ions into solution which shift the mercury dissolution wave and prevent the accurate determination of copper.



The square wave anodic stripping technique has proven to be a reliable, sensitive and accurate instrumental method for the detection of trace and ultra-trace levels of copper, lead, cadmium, and zinc in particulate-matter samples. Since the applications of square-wave polarography to trace analysis are numerous [92,97] it is recommended that further work be performed to extend the number of airborne metals that can be accurately determined by this technique.

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## VITA

Raul Mendez Merced was born on July 2, 1948 in New York City, New York to Raul Mendez Feliciano and Ana Teresa Merced de Mendez. He attended Nuestra Señora de la Merced High School in San Juan, Puerto Rico and graduated in May, 1966.

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