THE APPLICATION OF DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY FOR THE DETERMINATION OF COPPER, LEAD, ZINC AND CADMIUM IN AIRBORNE PARTICULATE MATTER.

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LIST OF ABBREVIATIONS

DPASV	Differential Pulse Anodic Stripping Voltammetry
ASV	Anodic Stripping Voltammetry
DME	Dropping Mercury Electrode
a.u.	arbitrary units
% RSD	Percentage Relative Standard Deviation

SUMMARY

An analytical method using Differential Pulse Anodic Stripping Voltammetry was developed for determining trace quantities of Cu, Pb, Cd and Zn in airborne particulate matter. The levels of the metallic pollutants were evaluated against meteorological data.

Instrumental parameters and sample processing were optimised for determining the metals in the concentration range 1 to 40 µg/l with a percentage relative standard deviation (%RSD) less than 10%.

Airborne particulate matter was decomposed by heating in a mixture of Hydrochloric and Sulphuric acids. Recovery studies were used to evaluate the digestion procedure, in the absence of a suitable reference material. The percentage recovery for the metals were between 95% and 100%. A total of 77 air samples were collected from January to December 1992, on the campus of the Peninsula Technikon. The samples were collected over 24 hour periods by filtration at a sampling rate of 20 liters per minute. The total average concentration for the metals was 25.3 $\mu g/m^3$. No Cd was detected in any of the samples.

CHAPTER 1

INTRODUCTION

1.1 HISTORICAL BACKGROUND OF VOLTAMMETRY

In the early 1920's J. Heyrovsky developed the technique of Polarography, from which the field of Voltammetry was developed. Whilst attempting to measure the amount of Copper plated onto a Platinum electrode Zbinden in 1931, found it extremely difficult to weigh accurately the small amount of Copper which plated out. He however, made a quantitative determination by measuring the amount of current consumed during the electrochemical stripping of Copper from the Platinum electrode. This was thus the birth of the concept of Stripping Analysis.

With the development of the Hanging Mercury Drop Electrode (HMDE) by W.Kemula in the early 1950's, Kemula and other workers emphasised the sensitivity attained with this technique, since Cadmium could then be determined below the parts per billion range. The rapid advancements made in electronics during the 1960's, coupled to a better understanding of the theoretical principles of stripping analysis, spurred the manufacture of low cost instruments and as a consequence, newer, more sensitive and more reliable procedures were developed in the 1970's, amongst which is Differential Pulse Anodic Stripping Voltammetry (DPASV).

The last ten to fifteen years were marked by the introduction of computer-operated instruments which generated automated, rapid and reliable results and further broadened the scope of Stripping analysis [1].

The low cost of instruments, the high sensitivity of the technique and the capability of determining more than one metal in a single sample solution, prompted scientists to apply the Anodic Stripping Voltammetry (ASV) technique to many diverse areas of analysis. Typical examples include the determination of trace quantities of metals such as Cu, Pb, Cd, Zn and Bi in ground and spring water [2], rain water [3,4], natural waters and atmospheric precipitation [5]. These metals have also been determined in clinical samples, namely blood [6], urine [7] and in various biological materials [8,9,10,11,12].

The presence of metals in suspended airborne metals which have been predominantly determined by Atomic Absorption spectroscopy [13,14,15] has also been successfully determined by Anodic Stripping Voltammetry (ASV) [16,17]. Since heavy metals are not biodegradable, they are retained indefinitely in the ecosystem and are considered to be the most harmful of pollutants. Some twenty years ago Colovos and co - workers developed an Anodic Stripping Voltammetric technique for determining Cd, Cu, Pb and Zn in airborne particulate matter. This procedure involved collecting the particulate matter by filtration onto a membrane filter (0.22 μm) and decomposing the sample by low-temperature ashing in a bomb. The results obtained were comparable to those obtained with Atomic Absorption Spectroscopy [17]. Harrison and Winchester successfully used Anodic Stripping Voltammetry for air pollution control studies [16], whilst other workers monitored air samples adjacent to highways where the suspended particulate matter comprised mainly of fuel combustion products [1]

Modern life demands of the Analyst to be able to determine trace amounts of metals in complicated sample matrices. However, trace metal analysis requires the successful contention in four analytical aspects, before valid results can be obtained. These are:

1. Achieving sufficient sensitivity of the method i.e. a sufficiently high signal to noise ratio. With the advent of computer operated analytical instruments and solid state electronics, analytical techniques such as Inductively Coupled Plasma Atomic Emission Spectrometry [18] and Flameless Atomic Absorption Spectrometry [15] are capable of sensitivities in the parts per billion range.

2. Achieving selectivity required to determine trace components of the system in the presence of other substances at several orders of magnitude higher; this problem is in many cases not solvable without the use of preliminary separation methods. The use of chelating agents for example Dithiazone [19], and Dimethylglyoxime [20], or in the form of ion-exchange resins [21], and the technique of liquid-liquid extraction [22] is often helpful in the separation and pre concentration of the metallic species.

3. Obtaining sufficiently pure chemicals so that the influence on the experimental results due to contamination is minimized.

4. Acquiring a skill for working with extremely dilute solutions, since losses of the analyte may readily occur through, for example, adsorption onto the walls of the vessels, hydrolysis, etc. [23].

1.2 POLAROGRAPHY AND VOLTAMMETRY

In Voltammetry a linearly increasing voltage is applied to the cell and the current generated is plotted as a function of the applied voltage. The current - voltage curves are called Voltammograms. The cell consists of:

1. an electrolyte solution containing the analyte,
2. a reference electrode and
3. an indicator electrode.

When the indicator electrode is a Dropping Mercury Electrode (DME) the technique is known as Polarography and the current-voltage curves are known as Polarograms. The voltage applied to the cell is measured relative to a standard reference electrode e.g. Saturated Calomel Electrode (SCE) **[24]**.

The Dropping Mercury Electrode consists of a glass capillary attached to a mercury reservoir. Drops of mercury fall from the capillary orifice at a constant rate of between 5-20 drops per minute. This technique is often called "Conventional" or "DC" (direct-current) polarography. DC polarography has a detection limit between 1 and 5×10^{-6} M, whereas other polarographic techniques, such as Differential Pulse Polarography, offer a lower detection limit, namely 1×10^{-8} M **[24]**.

1.2.1 DIFFERENTIAL PULSE POLAROGRAPHY

In Differential Pulse Polarography, a linearly increasing direct current voltage is applied to the cell, and as the mercury drop nears the end of its life a pulse with amplitude of 50 mV is superimposed onto the ramp voltage. The resultant current is measured at the start and end of the pulse; the difference in the current at the start and end of the pulse is plotted against the applied potential as a result the polarogram obtained is a peak shaped curve, having a maximum close to the Half Wave Potential [27]. Metals which form amalgams can be determined down to 1×10^{-9} M or even 1×10^{-10} M, by using Differential Pulse Polarography in combination with Anodic Stripping Voltammetry [24].

1.2.2 ANODIC STRIPPING VOLTAMMETRY

Anodic Stripping Voltammetry involves a combination of a concentration step and a stripping step. During the concentration step the solution is stirred or the electrode rotated. A controlled potential is then applied at the HMDE, at a potential more negative than the half wave potential of the metal ion. This leads to the reduction of the metal ion, thus forming an amalgam. The reduced reaction is allowed to take place over a fixed time period and under identical conditions. The concentration step is followed by the stripping step. In this step the stirring is stopped and the solution allowed to come to rest. The potential applied to the electrode is then reversed i.e. to potentials more positive than the half wave potential of the metal ion. As the applied potential reaches the half wave potential of the metal ion, oxidation of the amalgam occurs and the metal ion is stripped from the amalgam back into solution.

This stripping step is performed using any polarographic technique. When the polarographic technique is Differential Pulse Polarography, the technique is known as Differential Pulse Anodic Stripping Voltammetry (DPASV) [27]. The high sensitivity of the DPASV technique can be attributed to the high ratio of Faradaic to Non Faradaic currents generated in the electrochemical cell.

1.3 ELECTROCHEMICAL PROCESSES IN VOLTAMMETRY AND POLAROGRAPHY

1.3.1 FARADAIC AND NON-FARADAIC PROCESSES

Faradaic processes are those which involve the transfer of electrons across the electrode-solution-interface and obey Faraday's Law hence redox reactions are Faradaic processes. During these Faradaic processes a current, the Faradaic current, is generated. Its magnitude is governed by the mass transfer process, the technique being used, chemical kinetics, absorption, etc.

Non-Faradaic processes do not involve a transfer of electrons and hence do not obey Faraday's Law. These include processes where no charge transfer occur because they are thermodynamically or kinetically unfavourable, or where the structure of the electrode solution interface changes with changing potential or solution concentrations. Other Non-Faradaic processes are absorption and desorption at the electrode.

The Total current i_T which flows through the cell is the sum of the Faradaic and Non-Faradaic currents [27]

$$i_T = i_F + i_{NF}$$

1.3.2 MASS-TRANSFER PROCESSES

In voltammetry there are 3 common mass-transfer processes which occur. These are:

1. Diffusion under the influence of a concentration gradient,
2. migration of charged ions in an electric field and
3. convection currents due to the motion of the solution or the electrode.

Diffusion of the electroactive species towards the surface of the mercury is the only preferred transport process. All other modes of transport need to be eliminated or reduced to a minimum.

The supporting electrolyte used in voltammetry decreases the resistance of the solution and ensures that the electroactive species moves by diffusion and not electrical migration across the cell. The supporting electrolyte may be an inorganic salt (KCl, KNO_3, NaCl), or a mineral acid or base (HCl or NaOH). Where pH control of the solution is essential, buffer systems such as citrate - citric acid or acetate - acetic acid can be used. The ions of the electrolyte relieve the electric fields but do not undergo an electrochemical reaction.

The convection currents are reduced by not stirring the solution or rotating the electrode **[26]**.

The current generated by the supporting electrolyte arises from a Non-Faradaic process and is known as the Charging current.

1.3.3 CHARGING CURRENT

Even in the absence of reducible species in solution, a current must flow through the cell to charge the double layer capacitance at the surface of each new growing mercury drop. At the electrode-solution interface, charge separation takes place which causes the interface to behave as a capacitor and as a consequence a current is required to charge the capacitor; this current is called the Charging current. As the mercury drop grows and detaches itself from the electrode, so does the current flow through the system fluctuate. Thus the Charging current surges at the beginning of each drop when a new capacitor must be charged. The magnitude of these surges increases with applied potential, thereby producing a sloping baseline [25].

1.3.4 DIFFUSION CURRENT

The diffusion current arises from a Faradaic process. The Ilkovic equation is derived from the theory that the electroactive material is transported to the surface of the DME by diffusion only and not by other mass-transfer processes [25].

The maximum diffusion current is given by:

$$(id)av = 607\ n\ CD^{1/2}\ m^{2/3}\ t^{\ 1/6}$$

where;

id = the average current (in micro amperes) flowing during the life of a drop,

n = the number of equivalents per mole of the electrode reaction,

D = the diffusion coefficients of the electroactive substance in square centimeters per second,

C = the concentration of the electroactive material in millimoles per litre,

m = the mass flow rate of mercury through the capillary in milligrams per second,

t = the drop time in seconds.

The diffusion current is the difference between the current generated by the electroactive species in solution and the Charging current. Its magnitude is proportional to the concentration of active species in solution. The potential at which the current is half the magnitude of the diffusion current is the Half Wave Potential or E½. The E½ is independent of concentration and is a function of the oxidation-reduction characteristics of the species being evaluated. The E½ can be related to the Standard Electrode Potential (E^0) and is used for identification of species [24]. The high ratio Diffusion to Charging current is thus the major factor for attaining the low detection limits, thus making DPASV technique suitable for trace metal determinations.

1.4. GENERAL PRACTICAL CONSIDERATIONS

The purpose of this study is to develop an analytical procedure for determining trace amounts of Cd, Pb, Cu and Zn in airborne particulate matter. Furthermore, the influences of climatic factors on the concentrations of the metallic pollutants are to be evaluated on a qualitative basis.

Differential Pulse Anodic Stripping Voltammetry, like other analytical techniques is prone to problems which have to be addressed in order for creditable results to be obtained. Some of these problems are discussed below.

A difficulty encountered in polarography and voltammetry is the presence of dissolved oxygen in the analyte solution and must be removed prior to the application of the technique. Oxygen interferes with the analysis because it is electrochemically reducible, first to H_2O_2 and then subsequently to H_2O (thus producing large currents, which may react chemically with the analyte solutions). The reduction of oxygen is dependant on the pH of the solution.

First Step:

$O_2 + 2H^+ + 2e = H_2O_2$ (acidic medium)

$O_2 + 2H_2O + 2e = H_2O_2 + 2[OH]^-$ (neutral or basic medium)

Second Step:

$H_2O_2 + 2H^+ + 2e = 2\ H_2O$ (acidic medium)

$H_2O_2 + 2e = 2\ [OH]^-$ (neutral or basic medium)

The half wave potentials of the two step reduction of oxygen is observed at 0 and -1 Volt relative to the Saturated Calomel Electrode. The dissolved oxygen is removed from the analyte solution by bubbling high purity nitrogen gas through the solution for 5-20 minutes [1,24].

The mercury electrode has an anodic potential limit of +0.25 mV which occurs as a result of the oxidation of mercury. Hydrogen ions present in aqueous solutions are readily reduced and liberate hydrogen. The potential at which hydrogen is liberated is dependent upon the pH of the solution and there is a shift to a more positive potential of +59 mV per pH unit. Cu can be affected by the oxidation wave of mercury when making measurements at low pH in HCl medium, but the problem can be avoided by working in HNO_3 medium [4]. Zn determinations cannot be conducted at low pH since the reduction wave of hydrogen overlaps with the stripping peak of Zn, thus the pH of the sample solution must be adjusted to a pH greater or equal to 2 with an Ammonia-Ammonium Chloride buffer solution [11].

The sensitivity of the DPASV technique can be improved by increasing the deposition time, pulse amplitude, drop size, the stirring speed during the pre concentration step and by decreasing the pulse repetition time. However, the resolution decreases with increasing pulse amplitude, whereas with larger drops and higher stirring speeds the drop becomes unstable and falls off prematurely. The increase in deposition time may lead to the formation of inter metallic compounds. At lower scan speeds (10 mV/s) the resolution between peaks improve [28].

Variations which occur in the of rate of mass transfer to the HMDE during the pre concentration step, together with variations in the surface area of new drops forming, may result in non reproducible peaks. These variations can be corrected for by making use of an internal standard such as Indium [29]. Peak responses can be evaluated by making use of a calibration curve [30] or the method of standard additions. however, the presence of incompletely digested organic surface active material tend to be adsorbed at the electrode surface thus affecting the rate of the electrode process and consequently the current. This prohibits the use of calibration curves, but favours the use of the method of standard addition for evaluating the peak responses [7].

1.5.0 SAMPLE COLLECTION

In general, air samples may be collected in any area or location exposed to the atmosphere. Samples may be collected in a busy parking lot, along a highway or several meters above the ground. Air samples are collected to meet certain objectives such as:

1. to evaluate the quality of air to which a community is exposed;
2. to establish the influence of certain emissions from certain sources on the local quality of air;
3. the generation of information to assist in air pollution control management;
4. for research purposes such as the identification of chemical species from emission sources [31].

1.5.1 PARTICULATE POLLUTANTS

Particulate Pollutants are emitted by a great variety of sources, both stationary and mobile.

These pollutants are diverse in character and particle size varies from <0.1 µm to >100 µm. The major proportion of aerosols < 2µm are man made, including sulphates formed from sulphur dioxide oxidation and lead from vehicle exhausts. Particles of greater than 2 µm diameter are mostly natural (e.g. marine aerosol, wind blown soil). The division should not be regarded as rigid, since man made materials extends in size to >2 µm and natural airborne material to below this diameter.

Particulate pollutants may be sampled either from suspension in the air, by filtration for example, or by collection of deposited particles as they fall out from the atmosphere under gravitational influence, known as dustfall. Consequently, the study of particulate pollution is simplified by division of particles into two categories;

(a) **suspended matter** and

(b) **depositable matter.**

Metal pollutants are usually bound to suspended matter and may be collected by Filtration [31].

1.5.2 FILTRATION

Air is drawn through a network of small pores or openings using a suction pump. The filter medium may be a filter paper, sintered glass, a membrane or a granular medium such as carbon or diatomaceous earth. The types of filter papers commonly used are cellulose, glass fibre, membrane and nucleopore filters. The type of filter paper chosen is dependent upon its suitability for a particular application. The network of openings in glass fibre and cellulose filter papers are formed by the overlapping of fibres whereas the openings in membrane and nucleopore filter papers are pores of a controlled size (pore sizes less than 0.1 μm are available). Filter papers collect particles predominantly on their surfaces. As the air stream passes through the filter medium, particles are separated by various mechanisms such as:

1. Direct interception; the particles larger than the distances between the pores or the fibres are separated.

2. Diffusion; this is the most efficient way of collecting small particles (less than 0,4 µm), the particles diffuse from the air stream to the surface of the filter medium and adhere to the surface by means of attractive forces.

3. Impactions; particles of intermediate diameter are collected as the air flows through the pores, changes in the directions of the particles cause them to impinge on the internal surfaces and are lodged on these surfaces.

4. Electrostatic forces, high efficiencies may be achieved if the filter medium and the particles acquire static electrical charges.

The efficiency of the filter in capturing particles from the air being sampled is important in the selection of the filter medium. As the particles are deposited on the filter medium, the efficiency of sampling will vary with the velocity of filtration, the size of the particles and the amount of material already collected.

Low velocity sampling improve the collection of smaller particles by diffusion, whereas high sampling velocities decreases the efficiency of collection by diffusion, but increases the efficiency of collection by impaction. At very high sampling velocities the efficiency of collection may decrease due to the re-entrainment of particles previously deposited. Membrane and nucleopore filter papers are more suited than glass fibre and cellulose filter papers for collecting particles less than 0,6 µm. The high efficiency and low resistance to air flow, make glass fibre filter papers preferred, when using high volume air samples.

Generally the efficiency of sampling increases with the accumulation of particles over the filtering surface. The resistance to flow increases with the mass deposited, but at a rate smaller than the collection efficiency. In some cases it may not be desirable to use filters having a high efficiency, since higher head loss may occur, only low flow rates must be used and powerful sample pumps may be required.

The filter materials contain both major and minor contaminants. This may vary from one form to another. Ideally the filter medium used for sample collection should be free of or have negligible amounts of the particular compound to be determined. High blank concentrations in the filter paper result in large imprecision's in the analysis. Blank concentrations are critical during sampling of trace elements in the atmosphere. Membrane and nucleopore filter papers have a very low ash content and low levels of background impurities, thus making these filter papers well suited for sophisticated analytical work.

Blank filter contamination can be overcome by sampling larger volumes of air (e.g. increasing the sampling volume or increasing the sampling time) or by cleaning the filter media **[31]**.

1.6. SAMPLE PREPARATION METHODS

Most analytical techniques require the sample to be in solution form so that high sensitivity and better resolution may be obtained. However, samples are frequently obtained in the solid form and the analyte to be determined must be separated from the solid matrix and other species which may interfere with the analysis. Discussed below are some of the decomposition methods which have been used for the digestion of matrices prior to the application of the DPASV technique.

1.6.1 DRY ASHING METHOD

The sample 1-5 g is heated in the presence of air in an open vessel. Heating is done at a controlled temperature in a furnace. The vessels are usually made of platinum, silica or porcelain. This method is popular for the determination of trace metals. The furnace temperature is usually set between 500-550°C. Heating is continued until a fine ash is obtained, which is taken up into solution with an acid, filtered and the solution analysed. Decomposition is usually complete after 8-12 hrs. A major source of error with this method is the loss of volatile metals during the decomposition process. The method is advantageous in that the blank levels are low [32,33].

1.6.2 DRY ASHING WITH ADDITIVES

The efficiency of the dry ashing method is improved by the addition of an ashing aid such as H_2SO_4 or HNO_3. The additive is mixed with the sample prior to decomposition in the furnace. These ashing aids assist to accelerate oxidation, prevent the volatilisation of certain compounds, and prevents reaction between the compound and the crucible. When H_2SO_4 is used as an ashing aid volatile chlorides are converted into less volatile sulphates, thereby reducing losses of the metal species [32,33].

1.6.3 OXIDATION WITH HNO_3 AND H_2SO_4

A mixture of nitric and sulphuric acids is valuable for the destruction of the organic material. The mixture of acids is poured onto the sample and the sample heated between a temperature of 200-300°C. The nitric acid is added in excess (1 part H_2SO_4 and 10 part HNO_3). The sample is heated to dryness and allowed to cool. More nitric acid is added and heated further. The addition of nitric acid and heating may be repeated several times to ensure complete destruction of the organic material. Samples containing cadmium are not lost during this procedure but they are during the dry ashing method. The temperature of the digestion mixture must not exceed 350°C. Digestion is complete when the solution is clear. This method is suitable for breaking down organometallic metals for the determination of the metals. Heating the solution too vigorously must be avoided since splashing can occur which may lead to low recovery levels. The addition of a large excess of HNO_3 at the onset of the digestion procedure ensures that no charring occurs. The digestion method proceeds very rapidly as compared to dry ashing methods.

There are many variations of this method and other acids such as phosphoric, hydrofluoric, perchloric acids, etc can be used **[32,33,34]**.

1.6.4 OXIDATION WITH EXCITED OXYGEN

Oxygen at a pressure of 1-5 Torr, flows through a high frequency electric field and generate oxygen atoms. The oxygen is excited by a radio frequency source and flows onto the sample, which is placed close to the field. The temperature of the sample is about 200°C, thus this technique is often referred to as "low temperature ashing".

The reaction products and surplus atomic oxygen are pumped off and collected in traps. The temperature required for the ashing depends largely on the electrical power, oxygen pressure and on the nature of the sample.

Advantages of the technique are that several elements which are normally lost by conventional ashing procedures remain in the residue, because of the low temperature reaction between the metals and reaction vessels are minimised thus reducing contamination, higher recoveries of the metals are obtained.

Oxidation with excited oxygen is well suited for the determination of trace elements in organic materials. A disadvantage is that the low oxygen pressure results in a very slow rate of combustion, thus taking a long time (several hours to days) to burn off 1 gram of substance **[6,32]**.

1.6.5 DESTRUCTION IN A CLOSED VESSEL AT HIGH PRESSURE

Decomposition of the organic substances in the presence of oxygen may be carried out in a stainless steel bomb. The sample to be decomposed is crushed to a fine powder or pressed to form a pellet. The sample is then placed into a crucible made either of porcelain, silica or platinum, attached to the lid of the bomb. With the lid in place oxygen fills the bomb and the sample is electrically ignited by passing a current through a thin platinum wire which makes contact with the sample.

The advantages of such a technique are that substances which are resistant towards other digestion methods can be decomposed and the loss of metals through volatilisation are easily controlled. However, contamination from the bomb's ignition wire may occur, some material may be lost when excess oxygen is blown off after the combustion. The bomb must be left for approximately 2 hours before blowing off the excess oxygen **[7,17,32]**.

The diverse characteristics of different matrices and the variety of decomposition methods available emphasises the fact that there is no single standard decomposition method. Each of the digestion techniques discussed above have advantages and disadvantages which are intrinsic of the matrix that have to be digested. The preferred digestion method must destroy the matrix completely, with a minimum loss of the analyte and not introduce additional impurities into the sample. Such a digestion method is often chosen by trial and error and the equipment available.

CHAPTER 2

EXPERIMENTAL

2.0 INSTRUMENTATION

The determination of Cadmium, Lead, Copper and Zinc in airborne particulate matter was performed by the Differential Pulse Anodic Stripping Voltammetric technique.

The DPASV technique was performed with a polarographic analyzer (Amel model 433A) linked to an x-y plotter (Roland DXY-1100), a printer (Seikosha model SP-2000 Plus) and interfaced to a personal computer via an R232 cable. The working electrode was a hanging mercury drop electrode and a standard Ag-AgCl electrode filled with saturated KCl was used as the reference electrode; a platinum wire (1 mm in diameter and 5 mm long) served as the counter electrode. The various stages of the voltammetric technique were controlled by the software supplied by the manufacturers of the polarographic system.

The sample solution in the polarographic cell was de-aerated prior to the voltammetric determination by passing high purity nitrogen gas through the solution. A variable Gilson micropipet was used for adding the standard metal solutions into the electrochemical cell.

2.1 INSTRUMENTAL PARAMETERS

The metals present in the sample solution were determined individually using the following parameters:

Potential (mV)	**Cd**	**Pb**	**Cu**	**Zn**
Starting	-800	-600	-300	-1200
End	-300	-300	150	-800
Deposition	-800	-600	-300	-1200

OTHER GENERAL PARAMETERS

Current offset (%) = 0

Scan speed (mV/s) = 5

Pulse repetition (s) = 0.5

Pulse amplitude (mV) = 50

Pulse width (ms) = 40

Sampling time (s) = 10

Deposition time (s) = 180

Purge time (s) = 600

Stirrer speed (r.p.m.) = 300

Number of cycles = 2

Drop size (a.u) = 20

Delay before sweep (s) = 10

2.2 REAGENTS AND EQUIPMENT

Nitric Acid	65 %	Puranal	Riedel-de-Haen
Sulphuric Acid	98 %	Puranal	Riedel-de-Haen
Hydrochloric Acid	31 - 33 %	Puranal	Holpro Analytical
Ammonia	25 %	Analar	BDH

Buffer solutions (laboratory reagent, BDH):

(1) pH = 7.00 + 0.02

(2) pH = 4.00 + 0.02

Atomic Absorption Standard Solutions:

(1) Copper (1000 ppm)

(2) Lead (1000 ppm)

(3) Cadmium (1000 ppm)

(4) Zinc (1000 ppm)

Sierra air sampling unit

Millipore filter papers (0.22 um) Cat. No. GSWP 04700

Analytical balance AE 163 (Mettler)

Beckmann _31 pH meter

Corning general purpose combination electrode

Polyethylene scintillation vials (18 ml) were used as far as possible to store samples.

2.3 PURIFICATION OF WATER

High purity and Ultra high purity distilled de-ionised water were prepared as follows:

2.3.1 HIGH PURITY WATER (HPW)

The distilled water obtained from a Pyrex still (Fisons) was passed through a Milli-Q water purification unit, until a resistivity of 18 mega- Ohms was attained; this water was used for rinsing glassware and for preparing the 6 Molar nitric acid solution used for cleaning glassware.

2.3.2 ULTRA HIGH PURITY WATER (UHPW)

Ultra High Purity Water (UHPW) was prepared by passing High Purity Water (HPW) through an Elgastat UHQ water purification unit, until a resistivity of 18 Mega-ohms was attained. This water was used for the preparation of the electrolyte solution (0.1 M HCl), which in turn was used for preparing the sample and standard solutions.

2.3.3 CLEANING OF GLASSWARE

All glassware and plastic containers were cleaned by soaking them in a 6 Molar nitric acid solution for 1 week and then rinsing them thoroughly with high purity distilled de-ionised water.

2.4 STANDARD SOLUTIONS

Standard solutions were prepared in polyethylene scintillation vials, by diluting the atomic absorption standard solutions with the electrolyte as was necessary. Dilution of the solutions were done on a weight per weight basis using an analytical balance (Mettler AE 163). Standard solution concentrations ranged from 1 ppm to 30 ppm.

2.4.1 AMMONIA-AMMONIUM CHLORIDE BUFFER SOLUTIONS

10 Molar NH_3-NH_4Cl buffer solution was prepared by diluting Ammonia (25%) to 10 Molar with ultra high purity water and then adjusting the pH of this solution to 9.2 with Hydrochloric acid (31-33%). This solution was used to adjust the pH of sample solutions to between 2.1 and 3.00 prior to the determination of Zinc.

2.4.2 NITRIC ACID SOLUTION (6 MOLAR)

This solution was used for cleaning glassware and was prepared by diluting Nitric acid (65%) with high purity distilled de-ionised water on a volume per volume basis.

2.4.3 ELECTROLYTE SOLUTION (0.1 MOLAR HCL)

The electrolyte solution was prepared by diluting Hydrochloric acid (31-33%) with ultra high purity distilled de-ionised water on a volume per volume basis.

2.5 SAMPLE COLLECTION

Suspended airborne particulate matter was collected onto Millipore filter papers (0.22 µm). The filter papers were supported by a plastic mesh, thus preventing fragmenting of the papers.

Air samples were collected by drawing air through the filter papers at a rate of 20 liters per minute, using a Sierra air sampling unit. The air sampling unit was placed 40 meters from the main entrance gate of the Peninsula Technikon and positioned at a height of 1.5 meters above the ground. The entire sampling unit was locked in a steel casing, thereby preventing tampering with the instrument's settings. Air samples were collected over 24 hour periods commencing and ending at 5 pm. The filter papers were stored in petri dishes until they were ready for digestion.

All the meteorological data were supplied by the Weather Bureau at Pretoria. The meteorological conditions were recorded at the D F Malan weather station which is located at 33° 59' latitude and 36° longitude. This weather station is located 7 kilometers from the sampling site.

Minimum and maximum temperatures as well as rainfall were recorded at 8:00 hours. The wind speed, wind direction and relative humidity were recorded at 8:00, 14:00 and 20:00 hours daily and an average reading was calculated.

2.6 DIGESTION OF SAMPLES

2.6.1 DIGESTION METHOD 1

The sample, 0.5 ml Sulphuric acid (98%) and 5 ml Nitric acid were transferred to a 10 ml volumetric flask and heated in a sand bath set at 160 °C for 24 hours. The digested solution was made up to 10 ml with water and mixed well. A 3.0 ml aliquot of this solution was then transfered to the polarographic cell and made up to 10.0 ml with the electrolyte solution.

2.6.2 DIGESTION METHOD 2

The filter papers were digested according to a procedure described by Adeloju [32] and adjustments in the amounts of acids used and decomposition temperatures were made.

The filter paper was placed into a 125 ml Erlenmeyer flask and charged with 0.5 ml of Sulphuric acid (98%) and 5 ml of Nitric acid (65%). The flask and its contents were heated on a hot plate set between 250 °C and 270 °C until Nitrogen oxide fumes were given off. Two separate additions of 5.0 ml Nitric acid were made, cooling the flask for 3 minutes between additions. Heating was continued until all fumes dissappeared completely and the flask was allowed to cool to room temperature.

The filter papers dissolved within the first 2 minutes of heating, giving a dark grey coloured solution; as further additions of Nitric acid were made the solution became colourless. The total time required for complete digestion varied between 6 to 8 hours.

The contents in the flask was made up to 50 g with the electrolyte solution. The final solution was clear and colourless.

A 10 g aliquot of the sample solution was weighed into the polarographic cell and analyzed immediately.

2.7 SAMPLE ANALYSIS

A 10 g aliquot of the sample solution was weighed into the polarographic cell and de-aerated by bubbling high purity Nitrogen gas through the solution for 10 minutes. With the deposition potential set at -900 mV the sample was electrolyzed for 5 minutes and scanned over a voltage range from -900 to 150 mV. The presence of Cd, Pb and Cu were revealed by stripping peaks appearing at -680, -400 and -180 mV respectively. Each of the metals were then determined individually, using the prescibed instrumental parameters and were determined in the order Cd, Pb and Cu. The metals were quantified by the method of standard addition.

For the determination of Zinc, the pH of the sample solution was adjusted between 2.10 and 2.70 with 10 Molar Ammonia-Ammonium Chloride buffer solution (pH = 9.2) and analyzed using the prescribed instrumental parameters. The stripping peak of Zinc was observed at -1000 mV.

Carryover of metals from one sample run to another was prevented by rinsing the polarographic cell thoroughly with Ultra High purity water and then with the electrolyte solution. A blank run consisting only of a 10 g aliquot of the electrolyte solution was scanned from -900 to 150 mV and checked for spurious peaks before the next sample was analyzed.

2.8 QUANTITATION

The concentration of the analytes were determined by the method of standard additions. Peak height measurements were made from the baseline minima on each side of the stripping voltammogram to its maximum height **[29]**. Each measurement was made twice to ensure reproducibility, giving a total of 6 measurements; that is, two measurements before the addition of the standards and two measurements for each of the two standards added **[6]**. The concentration of analyte was calculated using the Standard Addition Formula:

$$C(unk) = \frac{C(std) \times i \times v \times 1000}{(i' - i) \times V + v}$$

where,

C(unk) = concentration of the final unknown solution.

C(std) = concentration of the standard solution.

V = volume of the sample solution.

v = volume of the standard solution added.

i = peak height of the unknown solution.

i' = peak height of the unknown solution + standard.

CHAPTER 3

RESULTS AND DISCUSSION

3.0 CONTAMINATION

Contamination can easily lead to extraneous results and therefore the levels of metallic contaminants were determined in both the electrolyte solutions and the filter papers.

The detection limit of the analytical method was governed by the amounts of Copper and Zinc present in the electrolyte solution and the filter paper, since no Cadmium or Lead were found in neither the electrolyte solutions nor the filter papers. The electrolyte solutions which were evaluated for contaminants, were prepared using two different grades of purified water, namely High Purity Water (HPW) and Ultra High Purity Water (UHPW). 10.0 ml aliquots of the electrolyte solutions were analyzed. Table 1 shows the differences in metallic concentrations between the two grades of water.

Table 1

High Purity Water (HPW)	
Copper (ppb)	**Zinc (ppb)**
7.08 ± 0.81	11.47 ± 1.98
5.30 ± 0.152	10.90 ± 0.56
Ultra High Purity Water (UHPW)	
Copper (ppb)	**Zinc (ppb)**
Not Detected	6.77 ± 0.061
Not Detected	6.25 ± 0.125

An average concentration of 6.51 ± 0.368 (ppb) was accepted for Zinc in Ultra High Purity water.

The filter papers were digested in sets of three according to Digestion Method 2 and the solutions were analyzed for metallic contaminants. Table 2 shows the variations in the filter papers, when High and Ultra High purity water were used to prepare electrolyte solutions.

Table 2

High Purity Water (HPW)	
Copper (ppb)	**Zinc (ppb)**
6.70 ± 0.603	30.74 ± 1.06
6.93 ± 0.79	33.61 ± 1.52
8.613 ± 0.362	28.32 ± 0.77
Ultra High Purity Water (UHPW)	
Copper (ppb)	**Zinc (ppb)**
Not Detected	13.16 ± 1.06
Not Detected	18.27 ± 0.311
Not Detected	18.18 ± 0.339
3.00 ± 0.55	32 40 ± 4.391

The results in Table 2 show that Zn was the major contaminant in the filter papers. Although there is a reduction in the amounts of Copper and Zinc, when Ultra High Purity Water was used, the possiblilty of an extraneous result appearing can not be ruled out, since variations between individual filter papers do occur. However, the values for Cu and Zn do not exceed 3 ppb and 33.61 ppb respectively for these metals.

3.1 RECOVERY STUDIES

In order to evaluate the accuracy of an analytical method, a suitable reference material of known metal concentration has to be subjected to the conditions set out by the analytical method. Adeloju [32] used reference materials such as animal muscle, bovine liver, oyster tissue and orchard leaves to compare the recovery of metals from several wet digestion and dry ashing methods suited speciffically for voltammetric trace metal analysis [32]. Ideally the matrix composition of the matrix of the sample and the reference material should be the same, so that any errors that may arise during the different stages of the analytical method may be realised and assessed.

However, for this study no suitable reference material could be obtained. Instead a recovery study of the metals from filter papers spiked with known amounts of metals was evaluated. The percentage recovery of the metals give an indication of the amount of metal released during the digestion procedure, which in turn indicates whether or not the matrix which traps the metal has been completely destroyed. The types of errors which may possibly arise from spiking a particular matrix with the analyte metals are; inaccuracies in the actual spiking procedure itself or adsorption onto the surfaces of the glass containers. Such errors lead to lower recovery percentages. Conversely, higher recovery percentages are an indication that contamination of the sample may have occured. Contamination of this nature generally occurs as a consequence of impure reagents or carryover.

An airborne metal pollutant collected onto a filter paper medium must be viewed as being surrounded by two matrices. The first being the organic or inorganic moiety to which the metal is attached; as in the case Alkyl Lead compounds. The second matrix is the filter paper itself onto which the metal pollutant is trapped. These matrices must be removed so that the metal alone is available for analysis.

Interferences which occur from contributions by the matrix show up as asymmetrical or distorted peaks in Voltammetric analysis.

Recovery studies using Digestion Methods 1 were performed and the recovery percentages of the metals from the reagents and filter papers. With this digestion method it was observed that a small volume of Sulphuric acid still remained in the volumetric flask after digestion. The remaining acid was made up to 10.0 ml with water. A 3.0 ml aliquot of this solution was then diluted to 10.0 ml with electrolyte solution and then analyzed.

Tables 3 and 4 show the recovery percentages which were obtained. The metals were determined simultaneously by scanning the sample solutions from -800 mV to 100 mV. Zinc was not used in these recovery studies, since its half wave potential (-1000 mV) occurs outside this voltage range; only the half wave potentials of Cadmium, Lead and Copper occur in this range and can thus be determined simultaneously. Furthermore, the pH of the solution was 1.1 which is not suitable for the determination of Zinc; a pH between 2.1 and 4.0 is required, since the reduction wave of Hydrogen overlaps with the stripping peak of Zinc at low pH values.

Table 3

Recoveries from Reagents

Number	**Metal**	**Spike** (ppb)	**Recovery** (ppb)	**Recovery** (%)
Blank 1	Cd	0.9	1.49	165.56
	Pb	0.9	0.76	84.44
	Cu	4.5	3.59	79.78
Blank 3	Cd	2.7	2.45	90.74
	Pb	2.7	2.53	93.70
	Cu	13.5	11.16	82.67
Blank 4	Cd	3.6	3.16	87.78
	Pb	3.6	2.6	72.22
	Cu	18.0	18.1	100.56
Blank 5	Cd	4.5	4.44	98.67
	Pb	4.5	4.5	100.0
	Cu	22.5	31.76	141.16

Table 4

Recoveries from Filter Papers

Number	Metal	Spike (ppb)	Recovery (ppb)	Recovery (%.)
Sample 1	Cd	0.9	1.54	171.11
	Pb	0.9	0.81	90.00
	Cu	4.5	6.93	154.00
Sample 3	Cd	2.7	2.53	93.70
	Pb	2.7	2.61	96.67
	Cu	13.5	15.52	114.96
Sample 4	Cd	3.6	3.28	91.11
	Pb	3.6	3.11	86.39
	Cu	18.0	17.52	97.33
Sample 5	Cd	4.5	4.12	91.56
	Pb	4.5	4.54	100.89
	Cu	22.5	25.91	115.16

Both sets of results show that extremely high recovery percentages were obtained at the low spiked concentrations for Cadmium and Copper. This can be attributed to contamination in the system, as a consequence of impure reagents or sample carryover. In the case of the Cadmium results the contamination is due to carry-over, since no Cadmium was detected in neither the reagents nor the filter papers. The contamination of Copper is largely due to the presence of this metal in the background electrolyte, since High Purity Water and not Ultra High Purity Water was used to prepare the electrolyte solution. However, the results in the above tables should be appreciated when working with extremely dilute solutions since the possibility of contamination errors occurring is large.

The results obtained in Tables 3 and 4 were calculated using the Standard Addition Formula. These results were compared to those obtained from Calibration Curves. The purpose of this comparison was to establish whether or not an agreement existed between the two quantitative methods. The calibration curves were set up by digesting a filter paper and making it up to 10 ml with water. A 3 ml aliquot of this solution was then diluted to 10.0 ml with electrolyte solution and transfered into the polarographic cell for analysis. The currents were recorded as 10 µl amounts of standard metal solutions were added to the bulk solution. Calibration curves such as those shown in the Appendix (Figures 1, 2 and 3) were generated for Copper, Lead and Cadmium. Table 5 shows the results obtained from the Calibration Curves and Standard Addition Formula.

Table 5

Standard Addition Formula vs Calibration Curve

Number	Metal	Formula (ppb)	Graph (ppb)	Percentage Deviation
Blank 1	Cd	1.49	1.21	18.79
	Pb	0.76	0.66	13.15
	Cu	3.59	4.55	26.74
Blank 3	Cd	2.45	2.12	13.47
	Pb	2.53	2.09	17.39
	Cu	11.16	10.31	7.62
Blank 4	Cd	3.12	3.02	3.21
	Pb	2.60	2.87	10.39
	Cu	18.10	17.63	2.60
Blank 5	Cd	4.44	4.12	7.21
	Pb	4.50	3.95	12.22
	Cu	31.76	20.29	36.11
Sample 1	Cd	1.54	1.21	21.42
	Pb	0.81	0.65	19.75
	Cu	6.95	7.71	10.94
Sample 3	Cd	2.53	2.60	2.76
	Pb	2.61	2.22	14.94
	Cu	15.52	15.02	3.33
Sample 4	Cd	3.28	3.02	7.93
	Pb	3.11	2.69	13.51
	Cu	17.52	16.6	5.25
Sample 5	Cd	4.12	4.12	0.00
	Pb	4.54	3.75	17.40
	Cu	25.91	20.29	21.69

At these low concentrations of metals there is good agreement between the two methods and the results show that measurement by either of the two quantitative methods are equally valid. Similar results were obtained by Komy [3] whilst determining metals in rain water, in the concentration range 0.15 to 50 ug/l. Since it was observed that the amount of residual Sulphuric acid remaining after digestion varied from sample to sample it is to be expected that the characteristics of the sample solution will also change. Thus variations in the results between the methods of quantitation are to be expected. However, from the agreement in the between the two quantitative methods it can be concluded that the destruction of the filter paper matrix was complete.

3.2 DIGESTION METHOD 1: APPLIED TO AIR SAMPLES

The airborne particulate matter which was collected onto filter papers were digested according to Digestion Method 1. The resulting solution after digestion was a dark grey coloured solution containing fine particles. This observation implied that the digestion was incomplete. When further additions of 2.0 ml of Nitric acid were made the dark grey solution eventually became colourless. The amount of Nitric acid added to the digestion solution varied from one sample to another and up to 8.0 ml of Nitric acid had to be added in some instances. This digestion method became time consuming and showed that the initial 5.0 ml Nitric acid added was insufficient for the complete destruction of the matrices. Another problem encountered with this method was that spot heating caused some of the volumetric flasks to crack, thus making this method unsuitable for analysis. This digestion method was not pusued further for the digestion of airborne particulate samples.

3.3 RECOVERY STUDIES: DIGESTION METHOD 2

Since it was observed that Digestion Method 1 was not suitable for the complete destruction of the airborne particulate matter matrices, recovery studies evaluating Digestion Method 2 had to be performed. In this digestion method a higher temperature and larger volumes of acids were used. Tables 6 and 7 show the recovery percentages of the metals from reagents and filter papers spiked with known concentrations of the metals. The metals were determined using the instrumental conditions set out in the experimental chapter.

Table 6

Recoveries from Reagents

Number	Metal	Spike (ppb)	Recovery (ppb)	(%) Recovered
Sample 1	Cd	8.82	9.48	107.48
	Pb	2.45	2.51	102.45
	Cu	18.93	20.22	106.81
	Zn	32.90	35.28	107.20
Sample 2	Cd	8.82	9.58	108.62
	Pb	2.45	2.51	102.45
	Cu	18.93	19.54	103.22
	Zn	32.90	33.50	101.82
Sample 3	Cd	8.94	8.55	95.64
	Pb	2.51	2.24	89.24
	Cu	19.54	20.36	104.19
	Zn	33.50	32.45	96.87
Sample 4	Cd	8.94	9.31	104.14
	Pb	2.16	2.19	101.39
	Cu	19.10	19.80	103.66
	Zn	32.95	33.80	102.58
Sample 5	Cd	8.73	8.90	101.94
	Pb	2.21	2.34	105.88
	Cu	18.5	19.18	103.68
	Zn	33.49	39.69	118.51
Sample 6	Cd	8.73	8.12	93.01
	Pb	2.21	2.25	101.81
	Cu	18.73	18.74	100.05
	Zn	33.49	38.45	114.81

Table 7

Recoveries from Filter Papers

Number	Metal	Spike (ppb)	Recovery (ppb)	Percentage Recovered
Sample 1	Cd	8.86	8.68	98.41
	Pb	2.17	2.25	103.69
	Cu	18.38	19.41	105.60
	Zn	33.10	36.46	110.15
Sample 2	Cd	8.86	8.60	97.07
	Pb	2.17	2.25	103.69
	Cu	18.38	20.04	109.03
	Zn	33.10	33.58	101.48
Sample 3	Cd	8.87	8.24	92.90
	Pb	2.27	2.27	100.00
	Cu	19.65	26.47	134.71
	Zn	32.91	32.86	99.85
Sample 4	Cd	8.87	8.24	92.90
	Pb	2.24	2.21	98.66
	Cu	19.65	19.35	98.68
	Zn	32.91	33.86	98.85
Sample 5	Cd	9.05	9.74	107.62
	Pb	2.22	2.35	105.86
	Cu	19.08	19.95	104.56
	Zn	32.78	37.70	115.01
Sample 6	Cd	9.05	9.95	109.94
	Pb	2.22	2.29	103.15
	Cu	19.08	19.57	102.57
	Zn	32.78	46.09	140.60

The values of 134.71% and 140.60% for Cu and Zn in Table 7 were rejected and the statistical analysis performed on the remaining data is given in Table 8.

Table 8

Recoveries from Reagents			
Metal	**Average (%)**	**Std. Dev**	**% RSD**
Cd	101.76	6.316	6.21
Pb	100.54	5.759	5.73
Cu	103.60	2.164	2.09
Zn	107.23	7.901	7.37
Recoveries From Filter Papers			
Metal	**Average (%)**	**Std. Dev**	**% RSD**
Cd	99.81	7.330	7.34
Pb	102.51	2.670	2.60
Cu	104.09	3.824	3.67
Zn	105.07	7.132	6.79

The results in Table 8 show that high recovery percentages with relative standard deviations below 10% are possible.

Adeloju **[32]**, studied the recovery of metals, from different matrices, using several digestion methods and found Digestion Method 2 gave recovery percentages between 95% to 100%. The results obtained here confirm his findings.

3.4 DIGESTION METHOD 2: APPLIED TO AIR SAMPLES

The digested sample solutions obtained by this method were colourless and showed no undigested matter, this could be attributed to the higher digestion temperature and the repeated additions of Nitric acid (5.0 ml aliquots). A typical voltammogram (scanned between -900 to 150 mV) for the electrolyte solution prior to sample analysis is shown in Figure 4 and the metals found in the sample solution are shown by Figures 5 - 7. The symmetrical peaks are an indication that the digestion of the matrices was complete. All airborne particulate samples were thus digested using this method. A scan of the background electrolyte was performed each time prior to the analysis of a new sample, in order to minimize contamination from sample carryover.

VOLTAMMOGRAM of ELECTROLYTE

10 ml of Electrolyte solution

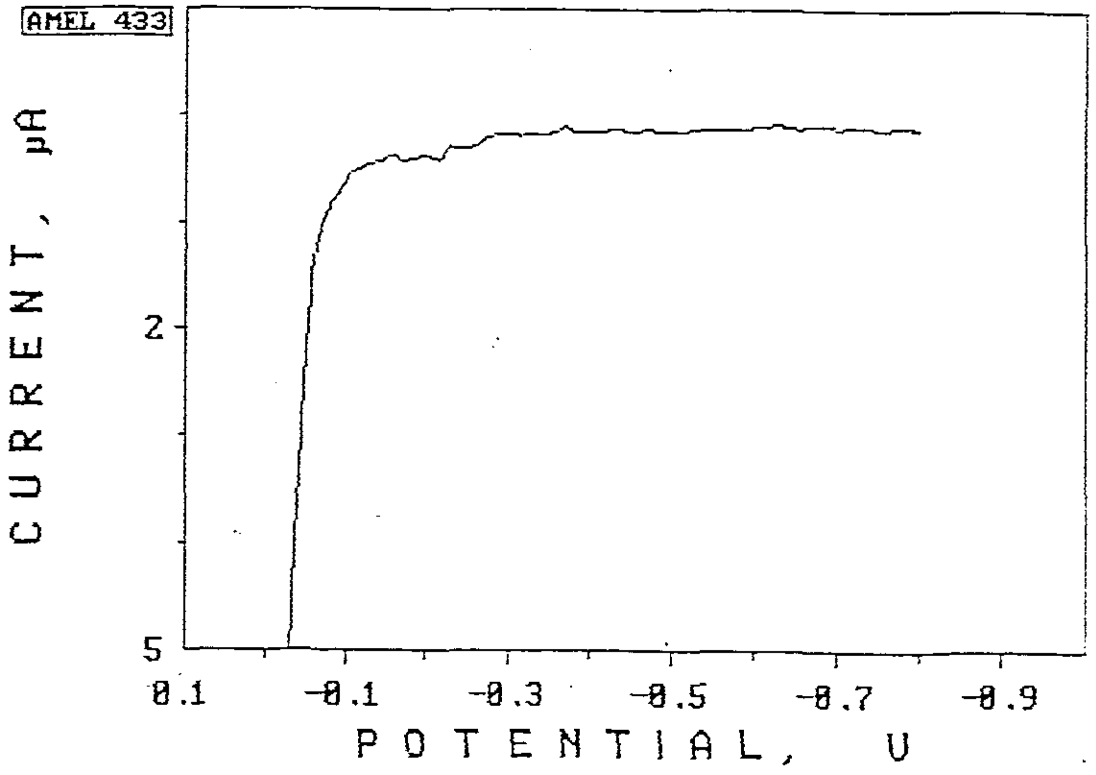

Figure 4

VOLTAMMOGRAM of COPPER

(1) 10.034 ml Sample solution
(2) 10.034 ml Sample solution + 18.64 ppb Cu
(3) 10.034 ml Sample solution + 37.27 ppb Cu

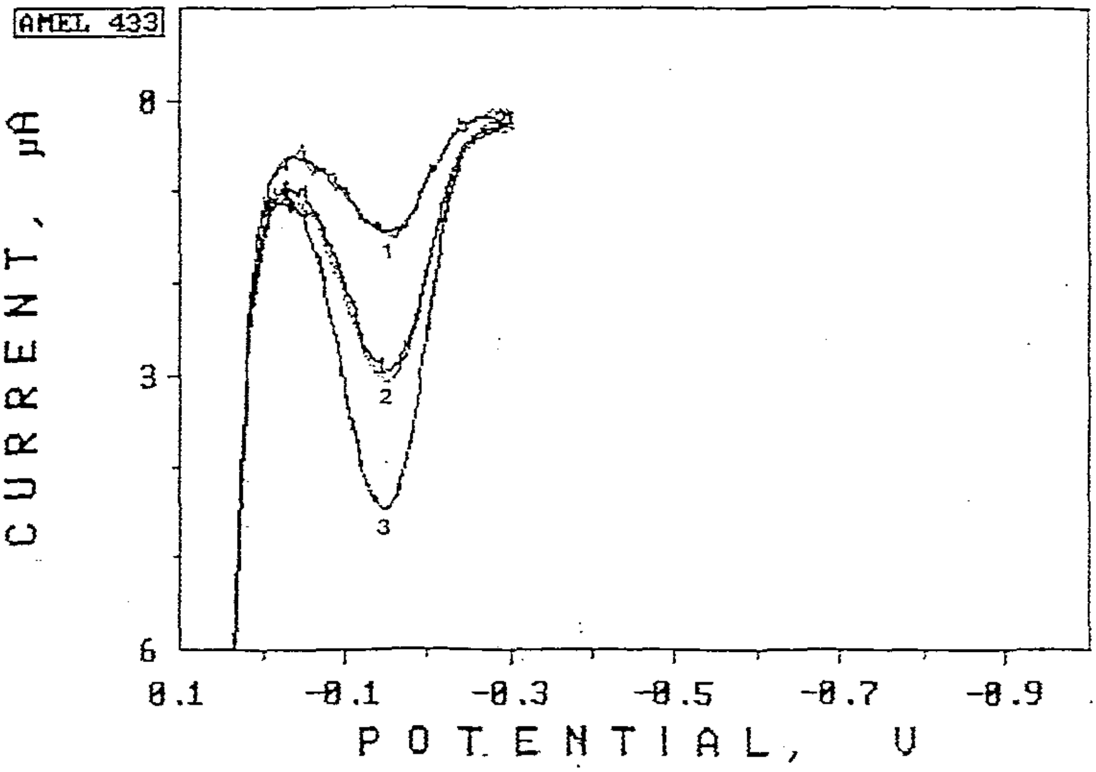

Figure 5

VOLTAMMOGRAM of LEAD

(1) 10.034 ml Sample solution
(2) 10.034 ml Sample solution + 10.29 ppb Pb
(3) 10.034 ml Sample solution + 20.58 ppb Pb

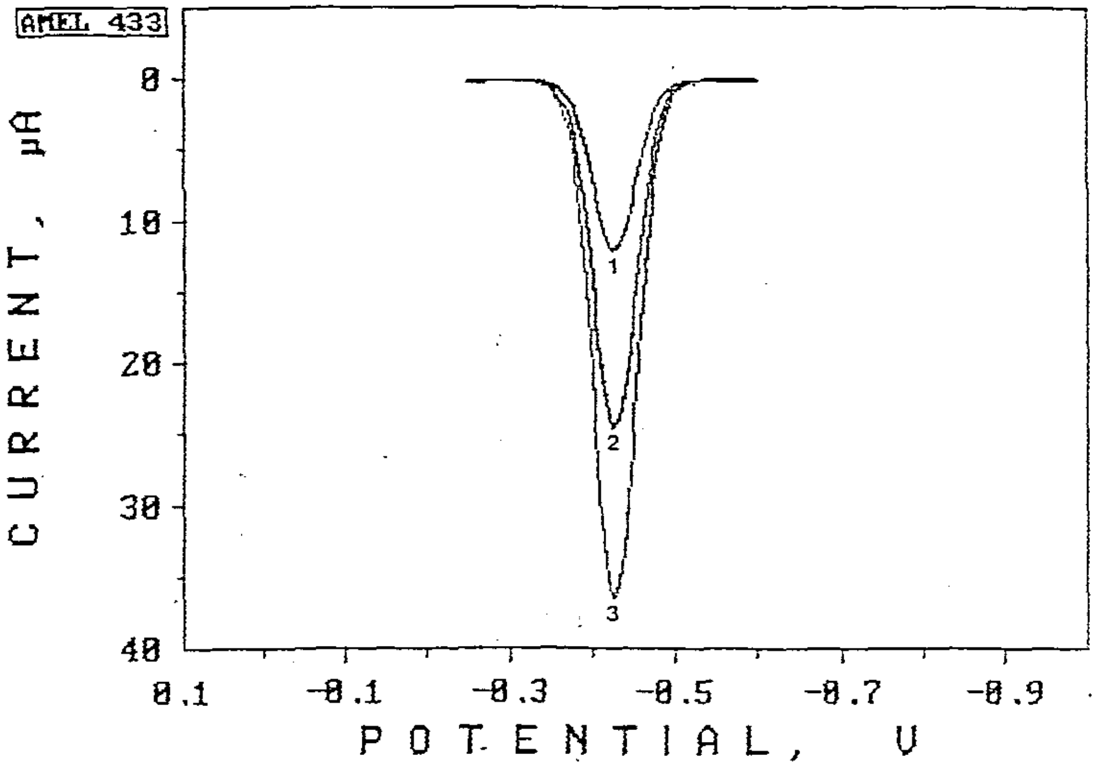

Figure 6

VOLTAMMOGRAM of ZINC

(1) 10.046 ml Sample solution
(2) 10.046 ml Sample solution + 60.12 ppb Zn
(3) 10.046 ml Sample solution + 120.23 ppb Zn

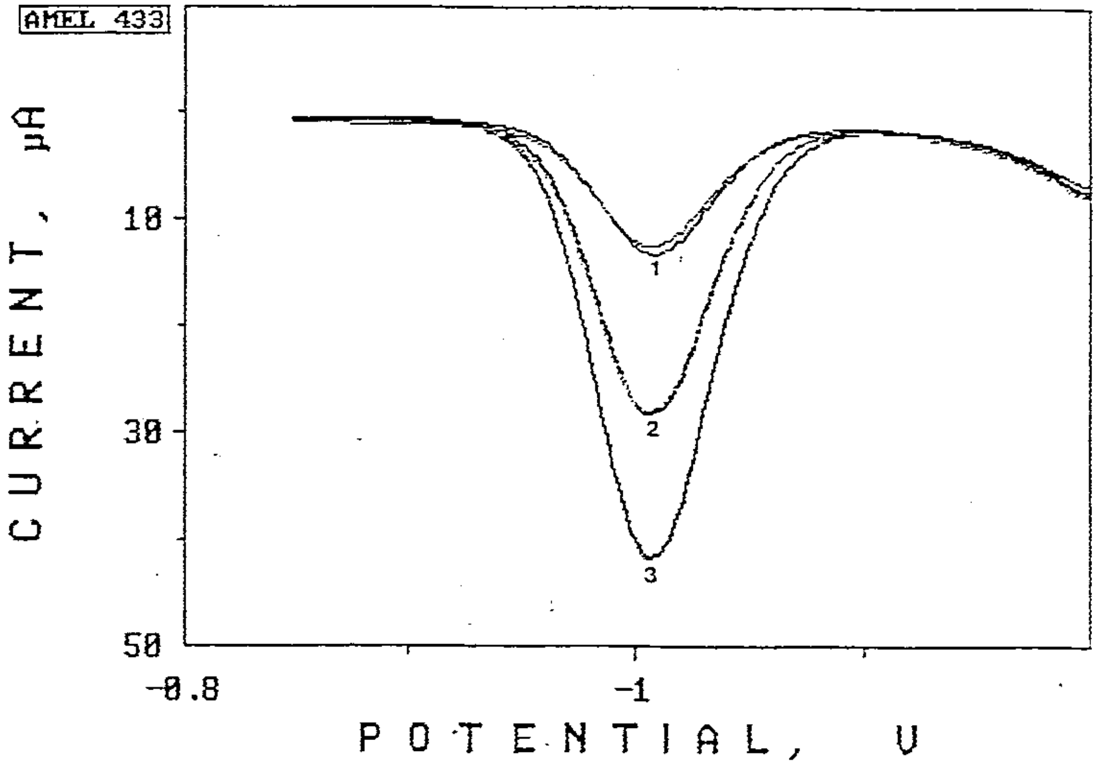

Figure 7

The Standard Addition Graphs in the Appendix (Figures 8, 9 and 10) were used to to calculate the concentrations of the metals from the voltammograms above. These results were compared to those calculated by using the Standard Addition Formula. Table 9 show the agreement in the results between the graphical method and the formula.

Table 9

Formula vs Graphical Method

Metal	Formula	Graphical Method
Cu	14.15 ppb	14.50 ppb
Pb	10.26 ppb	10.29 ppb
Zn	49.93 ppb	52.55 ppb

The concentration of the metal per cubic meter of air was calculated using the formula below:

$$\mathbf{Metal(ug/m^3) = C(unk) \times Factor \div 28.8\ m^3}$$

where, Factor = total sample volume (ml) ÷ volume of sample aliquot (ml)

The total sample volume of air collected over a 24 hour period was 28.8 m^3.

3.5 CONCENTRATION VARIATIONS OF METALLIC POLLUTANTS

The Differential Pulse Anodic Stripping Voltammetric technique procedure developed in the experimental section was used for the determination of airborne metals in the atmosphere.

Analyses were performed on 77 samples, which were collected randomly from February to December 1992. The samples were collected over a 24 hour period and thus reflect the daily averages of the metals detected. Air samples were not collected during January and June since the campus was closed for the summer and winter holidays. All samples were collected from one monitoring site which was located close to the main enterance gate of the campus. Since a high volume of motor vehicles passes through the gates daily, it is expected the metal pollutants are derived mainly from their emissions.

Copper, Lead and Zinc were the only metals that were detected; no Cadmium was detected in any of these samples. Table 10 shows the results obtained for these metals during the year 1992 and Figures 11 - 13 show graphical representations of the metals found in the samples.

Table 10

Date		Number	Cu (μg/m^3)	Pb (μg/m^3)	Zn (μg/m^3)
February	17-18	1	ND	2.13	24.69
	25-26	2	3.52	0.69	14.30
	26-27	3	4.88	2.35	35.16
	28-29	4	25.95	6.46	42.37
March	16-17	5	3.81	1.30	19.94
	23-24	6	6.46	2.03	19.59
April	13-14	7	ND	1.38	17.74
	22-23	8	ND	2.61	41.94
	23-24	9	ND	0.61	14.09
	28-29	10	3.48	2.39	ND
May	4-5	11	2.17	0.71	8.10
	5-6	12	6.3	1.92	31.55
	11-12	13	14.88	12.43	176.64
	12-13	14	14.88	7.55	123.26
	13-14	15	2.90	2.07	40.66
	14-15	16	2.31	0.87	15.71
	26-27	17	2.45	1.78	5.72
July	10-11	18	1.08	0.62	12.11
	13-14	19	1.21	1.00	10.74
	14-15	20	14.83	1.77	28.67
	17-18	21	1.24	0.30	9.19
	20-21	22	1.94	0.40	5.41
	22-23	23	2.26	0.44	8.98
	23-24	24	1.61	1.33	9.19
	27-28	25	1.11	0.91	ND
	28-29	26	1.10	0.77	7.87
	29-30	27	1.76	1.16	12.38

Date		Number	Cu ($\mu g/m^3$)	Pb ($\mu g/m^3$)	Zn ($\mu g/m^3$)
August	11-12	28	7.27	4.26	28.09
	12-13	29	2.35	1.59	15.51
	13-14	30	5.10	2.85	16.76
	15-17	31	1.88	2.55	8.63
	17-20	32	2.91	1.76	10.85
	21-24	33	1.23	0.58	8.63
	24-25	34	2.42	3.02	23.44
	29-31	35	3.32	3.31	20.93
September	1-2	36	1.81	2.05	53.55
	2-3	37	1.50	0.73	39.39
	3-4	38	1.95	0.59	10.34
	4-7	39	2.45	1.57	17.41
	7-8	40	1.87	0.98	14.51
	10-12	41	ND	0.92	8.51
	12-14	42	4.02	1.94	13.59
	14-15	43	4.04	1.11	21.47
	15-16	44	0.85	0.45	6.13
	17-18	45	2.67	1.11	23.64
	21-22	46	0.57	0.69	3.21
	22-23	47	2.18	2.13	16.71
	23-24	48	1.44	1.32	12.27
	24-25	49	1.89	0.92	6.10
	25-28	50	1.41	2.52	6.78
	28-29	51	1.45	0.52	3.72

Date		Number	Cu (μg/m^3)	Pb (μg/m^3)	Zn (μg/m^3)
October	30-(Sept) -1	52	1.23	0.82	7.95
	1-5	53	1.34	1.08	7.19
	5-6	54	1.85	1.06	31.05
	7-8	55	1.57	0.48	6.46
	8-10	56	1.05	1.05	8.65
	10-12	57	0.81	0.55	3.71
	12-13	58	1.09	0.89	30.15
	13-14	59	1.67	0.89	14.08
	14-15	60	0.77	0.21	0.44
	15-19	61	0.82	ND	2.95
	19-20	62	1.45	0.43	5.94
	20-21	63	1.06	0.43	5.97
	21-22	64	1.32	0.49	11.05
	22-23	65	0.97	0.43	6.95
	26-27	66	1.30	0.9	10.71
November	17-18	67	1.20	0.8	10.62
	19-20	68	1.07	0.46	5.34
	20-23	69	0.96	3.19	4.44
	23-24	70	1.30	0.55	6.45
	24-25	71	1.13	0.34	11.60
	25-26	72	1.13	0.83	6.74
	26-27	73	2.06	0.89	8.54
December	1-2	74	0.8	0.17	ND
	2-3	75	1.12	0.59	3.95
	7-8	76	ND	0.33	5.56
	8-9	77	0.49	0.33	23.35

CONCENTRATION PROFILE of COPPER

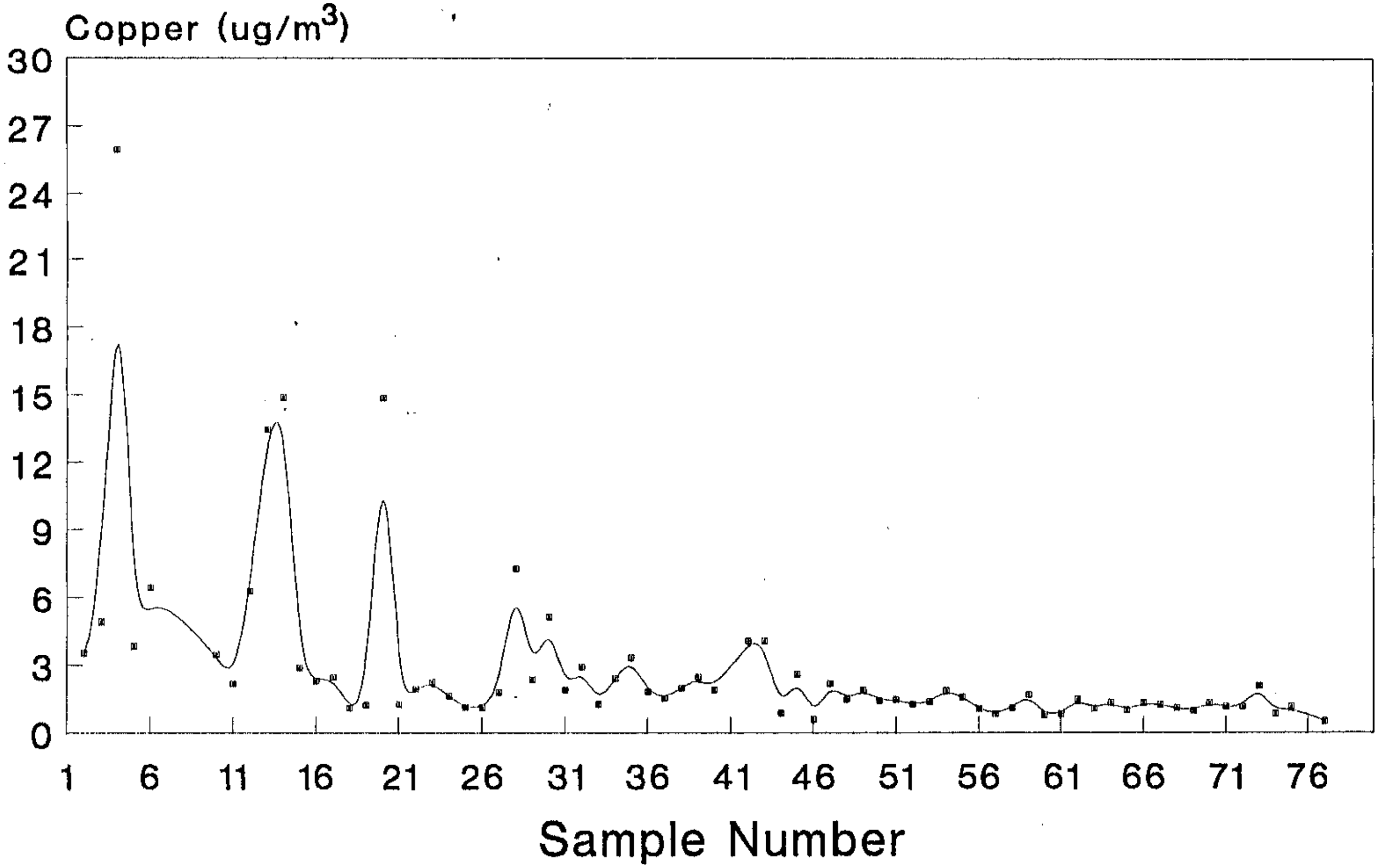

FIGURE 11

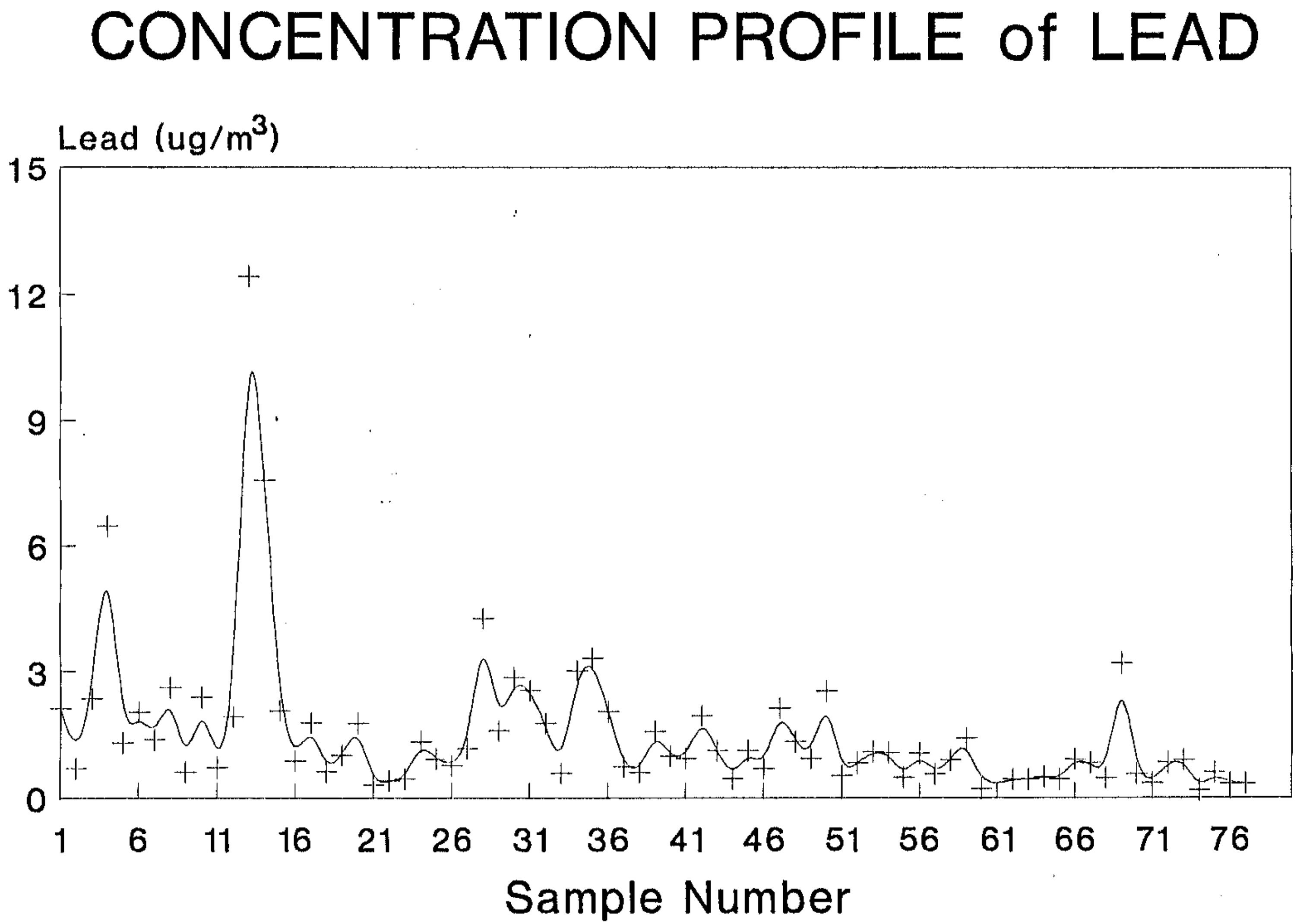
CONCENTRATION PROFILE of LEAD
Lead (ug/m^3)
15
12
9
6
3
0
1
6
11
16
21
26
31
36
41
46
51
56
61
66
71
76
Sample Number

FIGURE 12

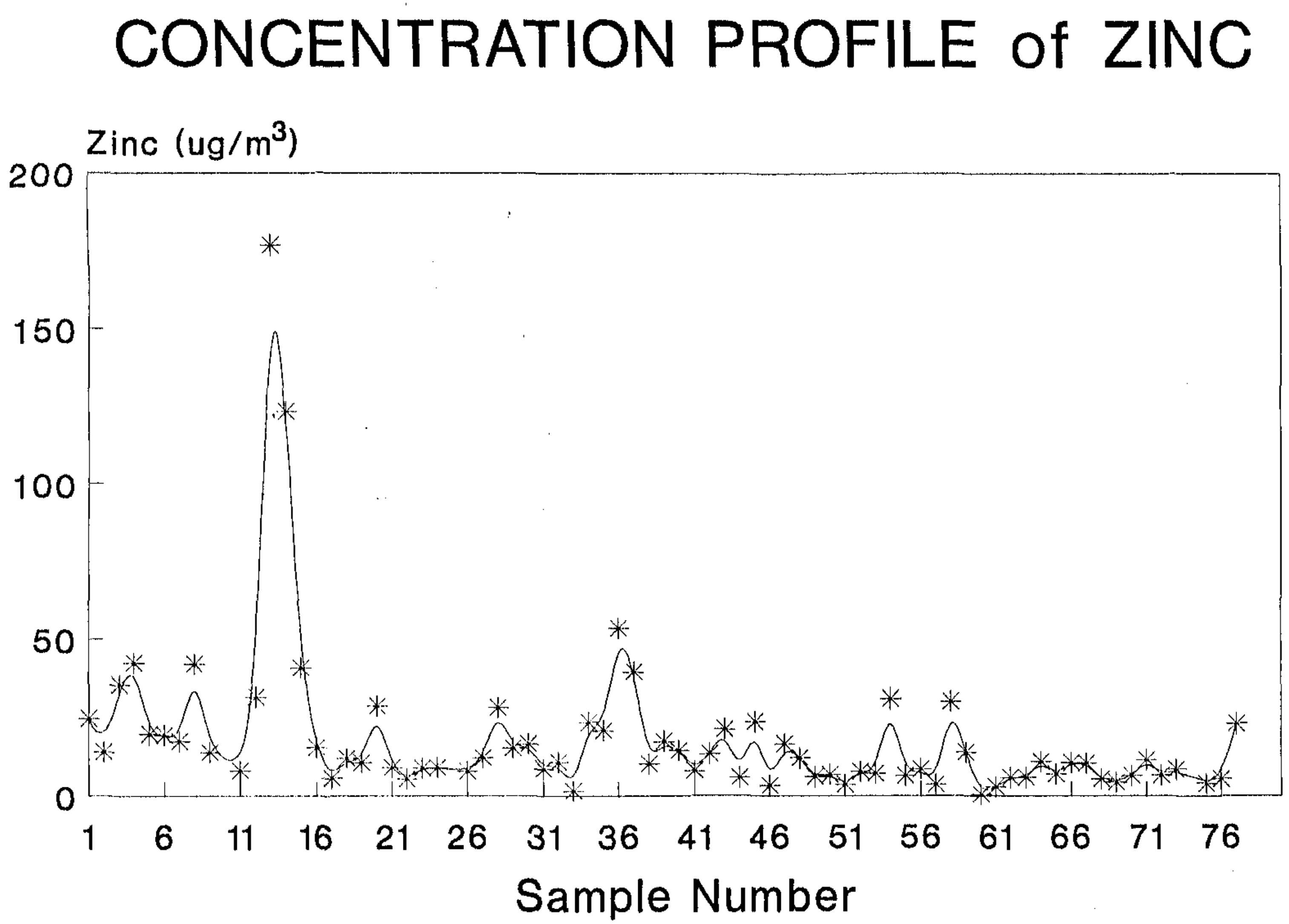
CONCENTRATION PROFILE of ZINC
Zinc (ug/m^3)
200
150
100
50
0
1
6
11
16
21
26
31
36
41
46
51
56
61
66
71
76
Sample Number

FIGURE 13

The positions at which peaks occur relative to the sample number are tabulated in Table 11. The positive and negative signs indicate the presence and absence of peaks.

Table 11

Sample Number	Copper	Lead	Zinc
1-6	+	+	+
11-16	+	+	+
18-21	+	+	+
26-31	+	+	+
33-36	+	+	+
41-46	+	+	+
46-51	-	+	+
51-56	-	+	+
56-61	-	+	+

These plots show that the peaks and troughs of the metals coincide closely with each other, thereby indicating that the metals are emitted from a common source, namely the emissions from motor vehicle exhaust systems. Analysis of exhaust gas by Atomic Absorption Spectroscopy showed that Cu and Zn are also emitted from motor vehicle exhaust systems [37].

The average concentrations and standard deviations for the metals as determined for the year 1992 are therefore; Cu (3.77 ± 3.23), Pb (1.69 ± 1.11) and Zn (20.31 ± 14.7) micrograms per cubic meter. Since the standard deviation indicates the distribution about the mean it can be deduced that there is more than one factor contributing towards the concentration of metals found in the atmosphere. These factors can include the volume of traffic flow and or the climatic conditions.

3.6 MONTHLY METAL AVERAGES

The monthly average concentrations of the metals are given in Table 12 and represented graphically by the bar graph in Figure 14.

Table 12

Month	Cu ($\mu g/m^3$)	Pb ($\mu g/m^3$)	Zn ($\mu g/m^3$)	Total ($\mu g/m^3$)
1				
2	11.5	2.9	29.1	43.5
3	5.1	1.7	19.8	23.6
4	3.48	1.7	24.6	29.8
5	6.3	3.9	57.4	67.6
6				
7	2.8	0.9	11.6	15.3
8	3.3	2.5	15.7	21.5
9	2.0	1.2	16.1	19.3
10	1.2	0.7	10.2	12.1
11	1.26	1.01	7.68	10.0
12	0.80	0.36	10.95	12.1
Average	3.77	1.69	20.31	25.6
Std. Dev.	3.23	1.11	14.7	17.87

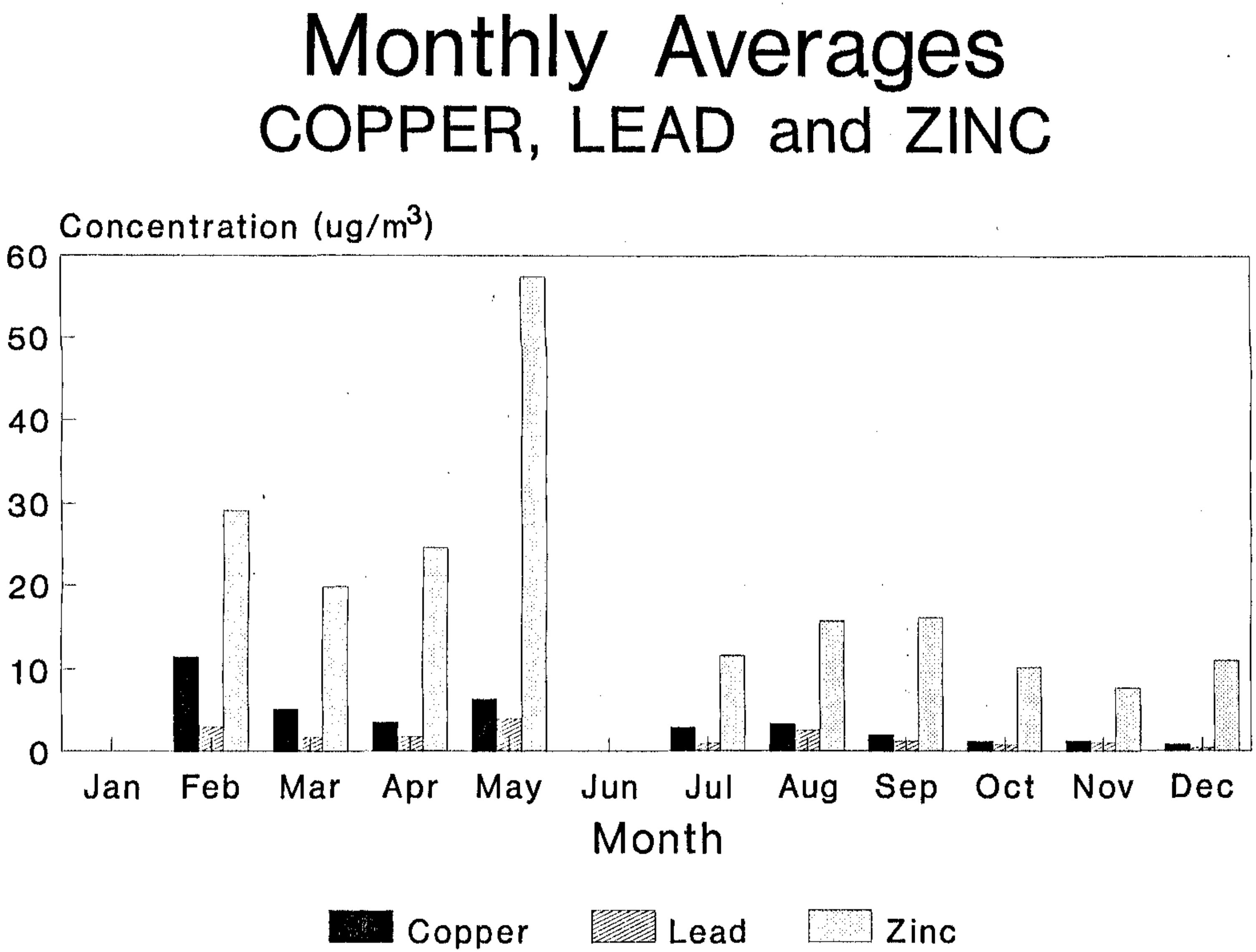
Monthly Averages
COPPER, LEAD and ZINC

FIGURE 14

Higher concentrations of metal were found during the first half of the year than during the second half. February showed an a extremely high Cu result; this high value was as a consequence of a veld fire which occured close to the campus on the 28-29th of February. Cu is released during the combustion of plant material.

The total concentration of the metals for each month is shown in Figure 15. Since it is not possible to obtained a true average background concentration for the metals, the yearly average was used for this purpose (Average 25.6 $\mu g/m^3$), thus the increase or decrease in the metal concentrations during the year were compared relative to this average.

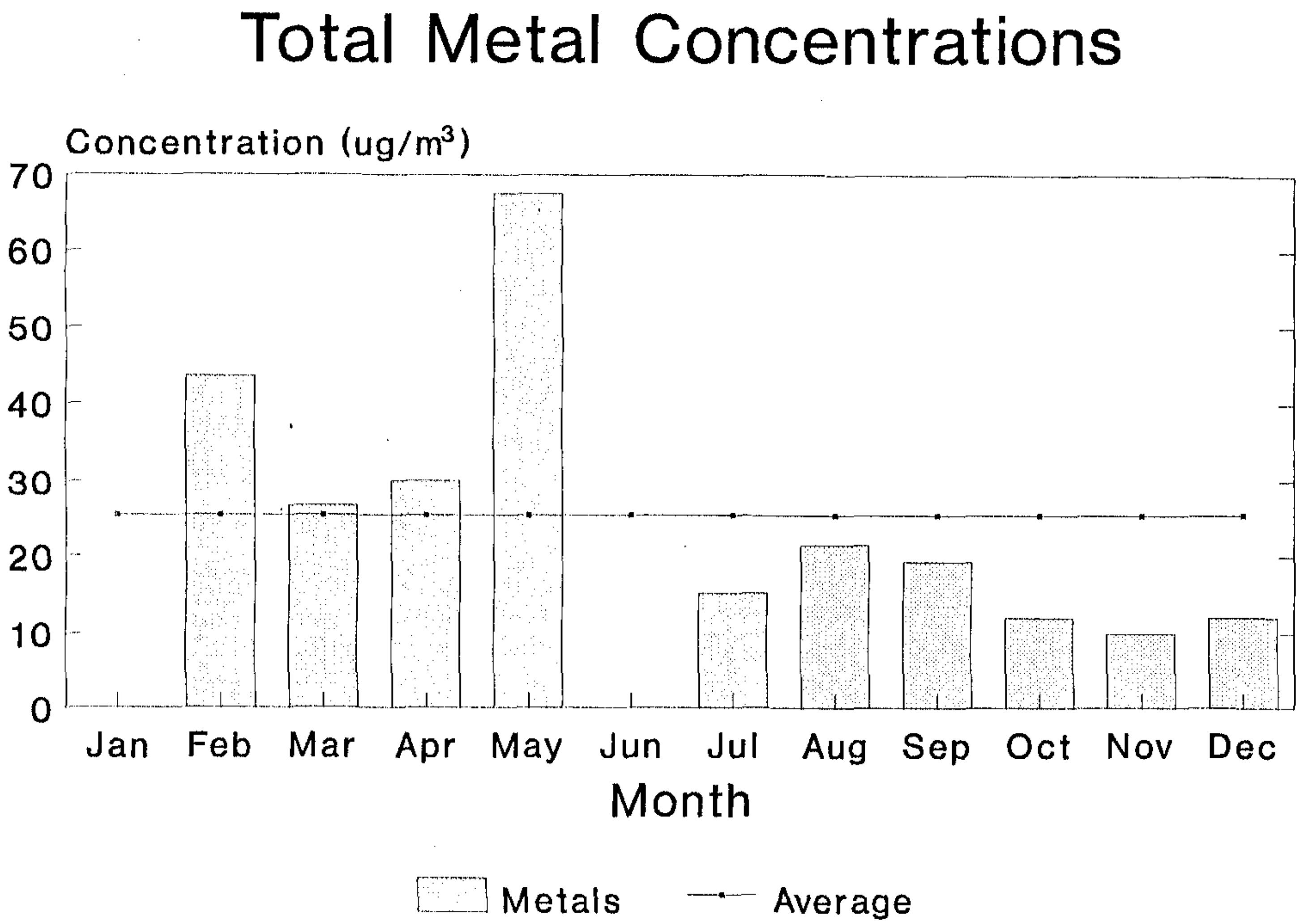
Total Metal Concentrations
Concentration (ug/m³)
70
60
50
40
30
20
10
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month
Metals
Average

FIGURE 15

The variations in metal concentrations with different periods show that there are factors which attribute towards this phenomenon. It is well known that the atmosphere uses meteorological mechanisms which aid in the removal of pollutants. These mechanisms include stirring or turbulant diffusion, photochemical transformations, by rainout or fallout [36].

3.7 METEOROLOGICAL DATA FOR 1992

The concentration of the metal pollutants was plotted against the meteorological data, (temperature, wind speed, relative humidity and rainfall) in order to establish whether or not any trends exist between the data. Figures 16 to 19 show the plots obtained and the meteorological data are shown in Tables 13 to 15.

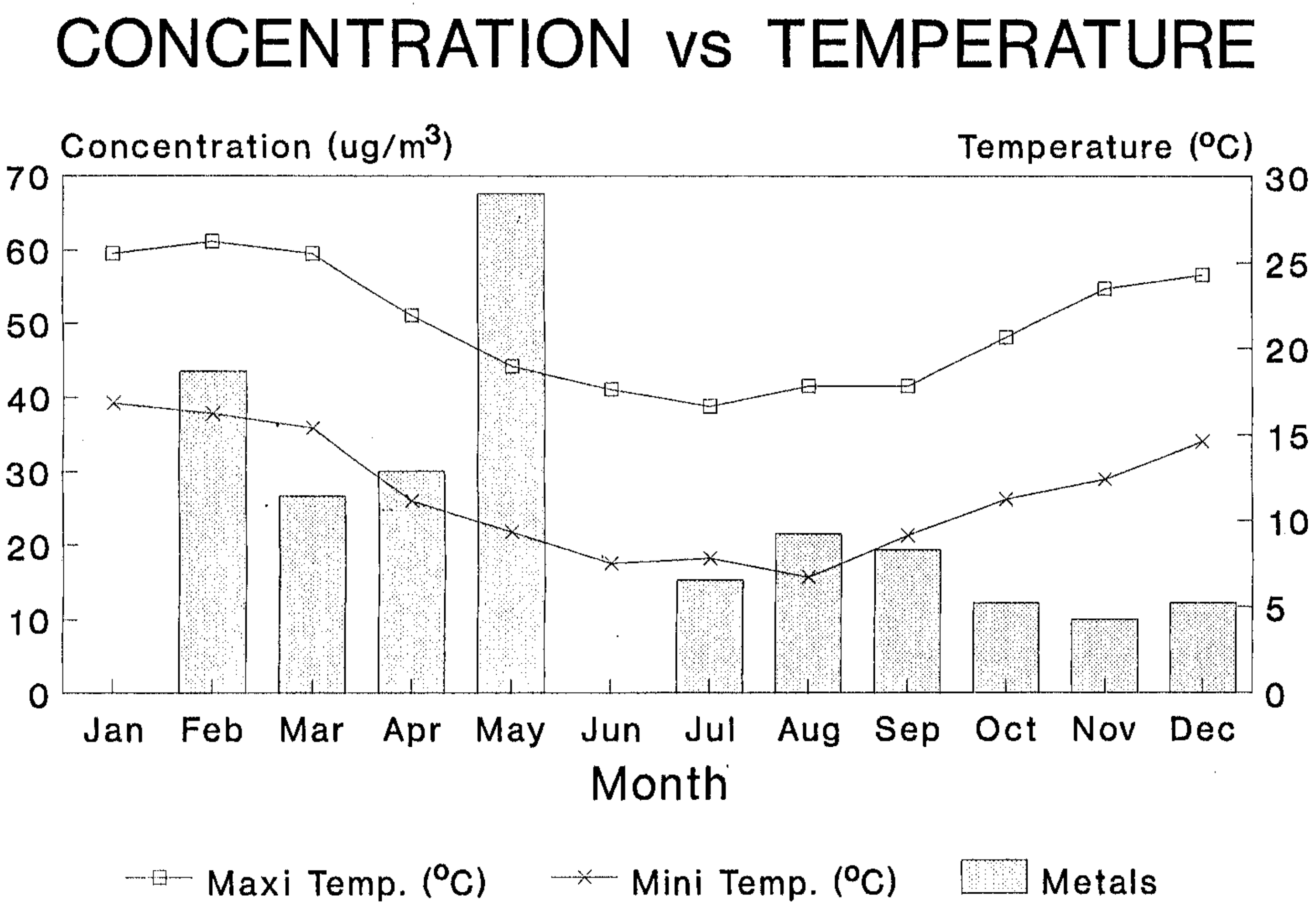
CONCENTRATION vs TEMPERATURE
Concentration (ug/m3)
Temperature (°C)
70
60
50
40
30
20
10
0
30
25
20
15
10
5
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month
Maxi Temp. (°C)
Mini Temp. (°C)
Metals

FIGURE 16

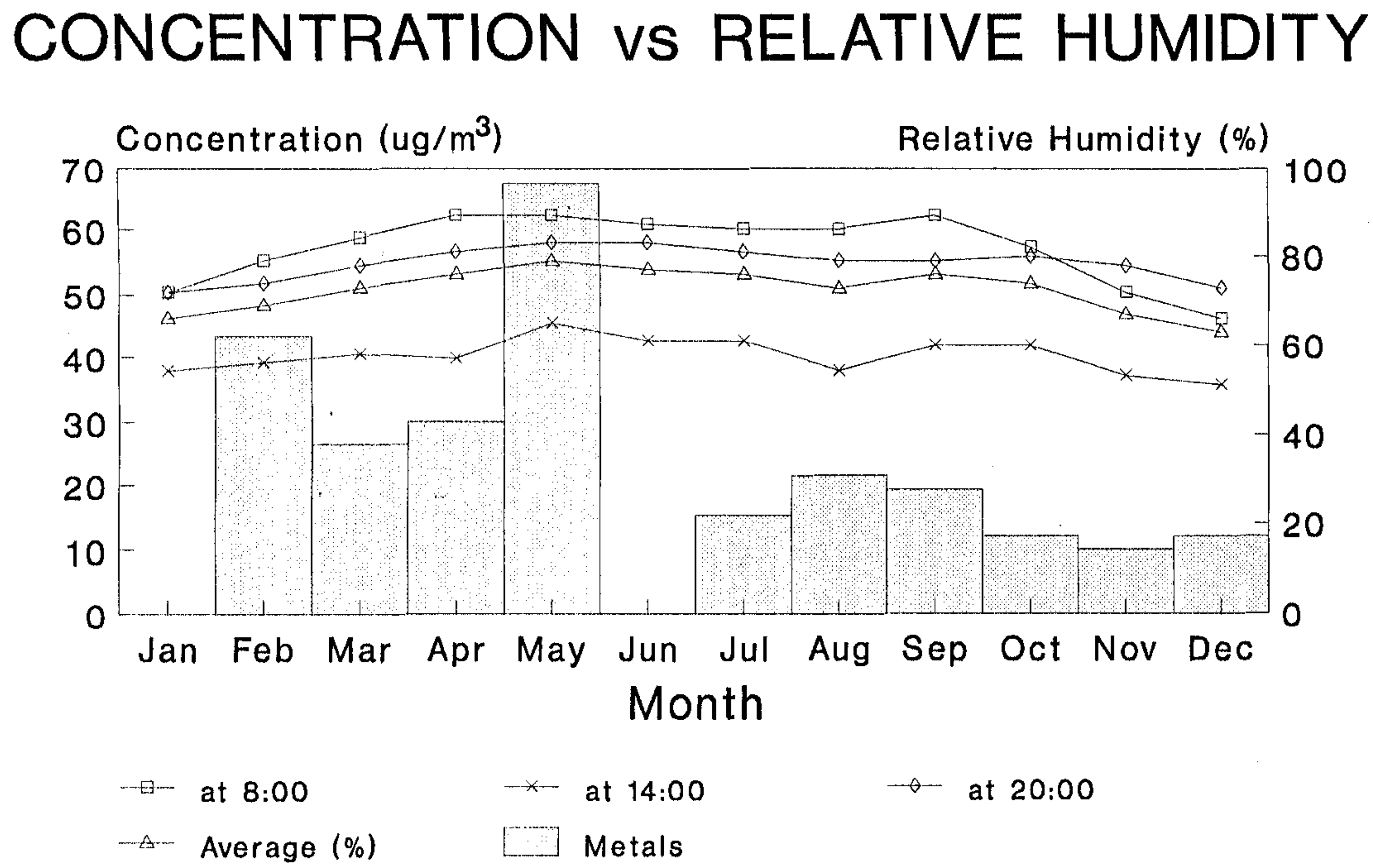
CONCENTRATION vs RELATIVE HUMIDITY
Concentration (ug/m3)
Relative Humidity (%)
70
60
50
40
30
20
10
0
100
80
60
40
20
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month
at 8:00
at 14:00
at 20:00
Average (%)
Metals

FIGURE 17

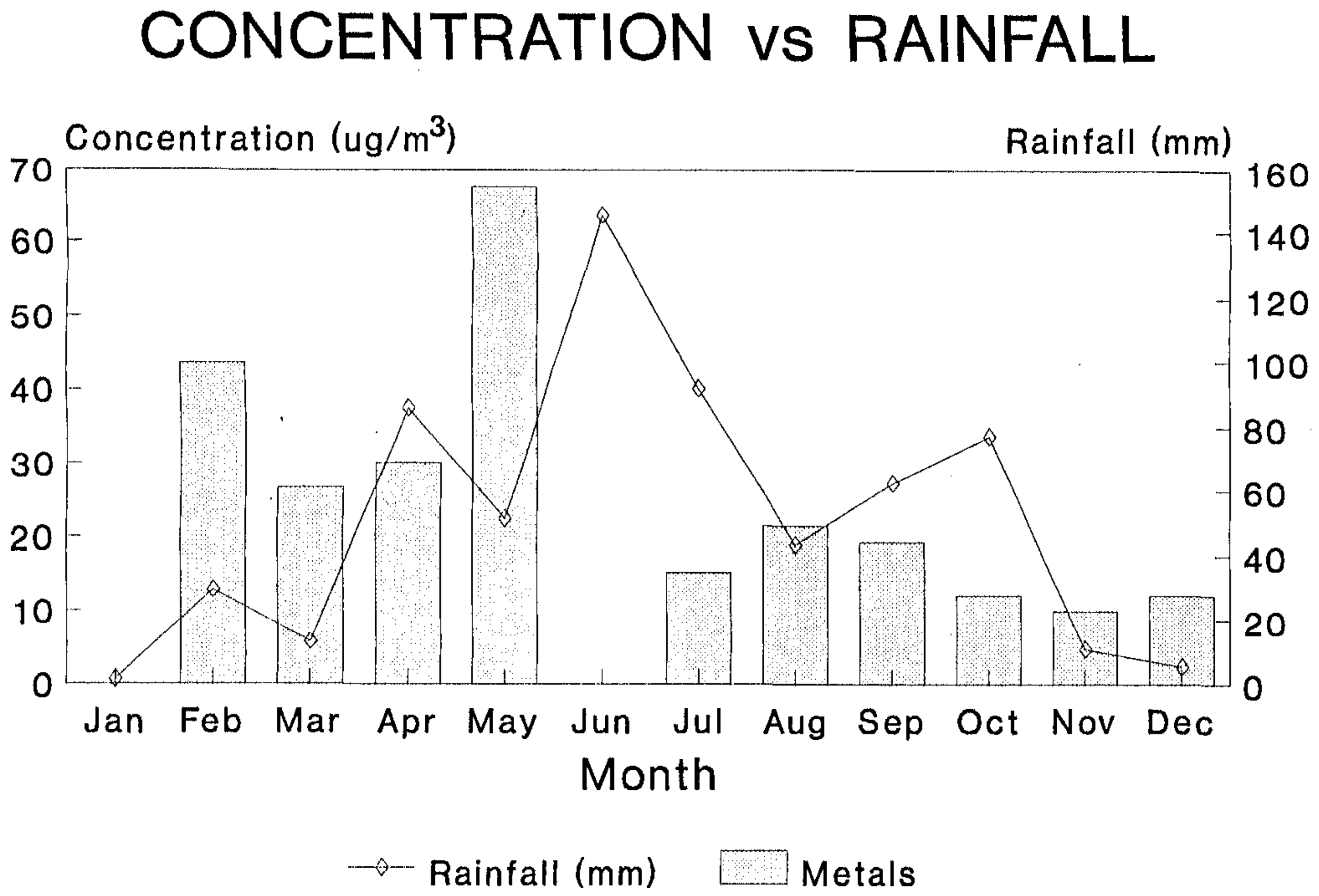
CONCENTRATION vs RAINFALL
Concentration (ug/m3)
Rainfall (mm)
70
60
50
40
30
20
10
0
160
140
120
100
80
60
40
20
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month
Rainfall (mm)
Metals

FIGURE 18

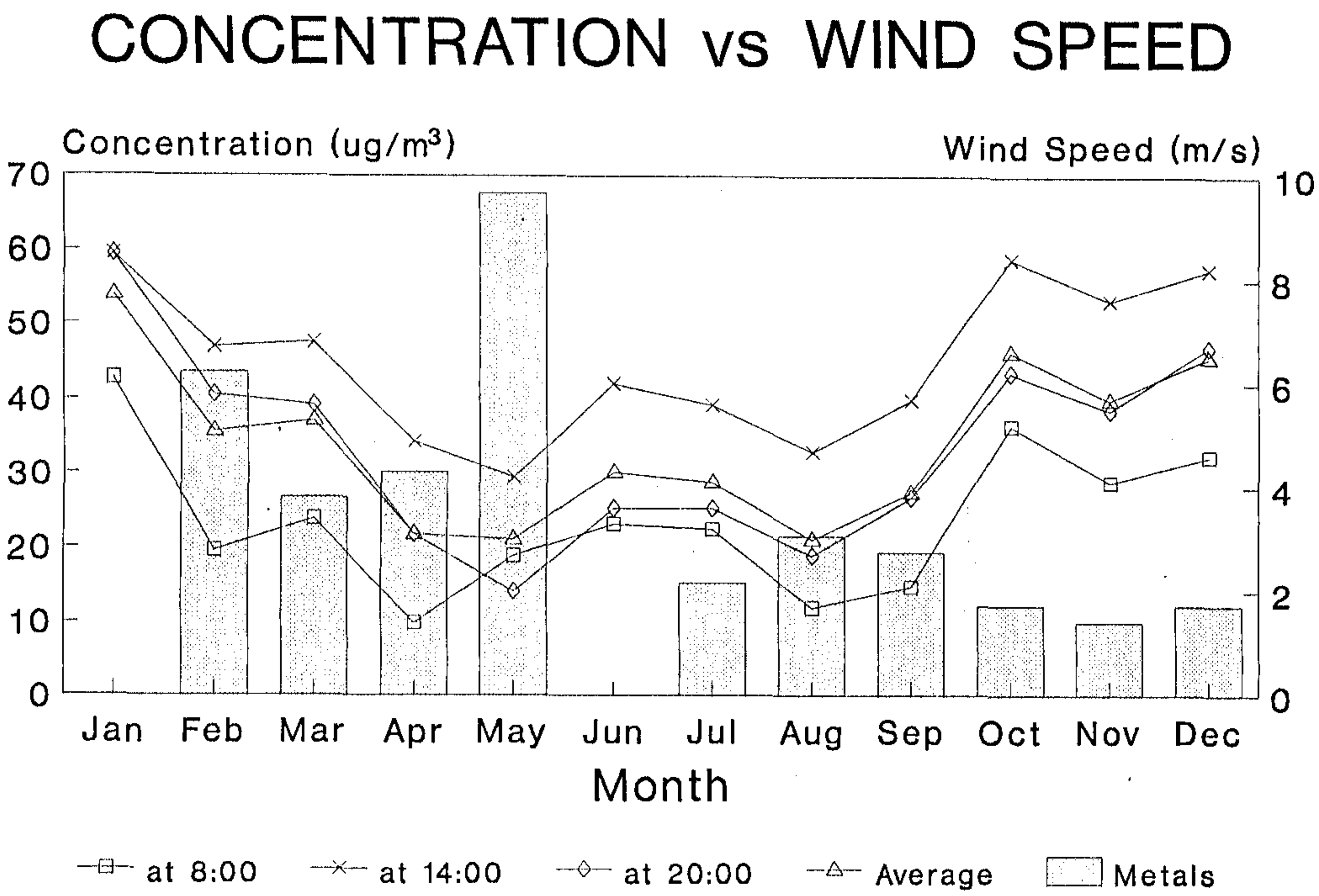
CONCENTRATION vs WIND SPEED
Concentration (ug/m³)
Wind Speed (m/s)
70
60
50
40
30
20
10
0
10
8
6
4
2
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month
at 8:00
at 14:00
at 20:00
Average
Metals

FIGURE 19

Table 13

	Relative Humidity (%.)			
Month	**8:00**	**14:00**	**20:00**	**Average**
January	72	54	72	66
February	79	56	74	69
March	84	58	78	73
April	89	57	81	76
May	89	65	83	79
June	87	61	83	77
July	86	61	81	76
August	86	54	79	73
September	89	60	79	76
October	82	60	80	74
November	72	53	78	67
December	66	51	73	63

Table 14

	Wind Speed (m/s)			
Month	**8:00**	**14:00**	**20:00**	**Average**
January	6.1	8.5	8.5	7.7
February	2.8	6.7	5.8	5.1
March	3.4	6.8	5.6	5.3
April	1.4	4.9	3.1	3.1
May	2.7	4.2	2.0	3.0
June	3.3	6.0	3.6	4.3
July	3.2	5.6	3.6	4.1
August	1.7	4.7	2.7	3.0
September	2.1	5.7	3.8	3.9
October	5.2	8.4	6.2	6.6
November	4.1	7.6	5.5	5.7
December	4.6	8.2	6.7	6.5

Table 15

	Temperature (°C)		
Month	**Minimum**	**Maximum**	**Rainfall (mm)**
January	16.8	25.5	1.4
February	16.2	26.2	29.5
March	15.4	25.5	13.0
April	11.1	21.9	85.8
May	9.3	18.9	51.2
June	7.5	17.6	145.1
July	7.8	16.6	91.7
August	6.7	17.8	43.3
September	9.1	17.8	62.3
October	11.2	20.6	77.1
November	12.4	23.5	10.7
December	14.6	24.3	5.2

3.8 METEOROLOGICAL FACTORS INFLUENCING AIR POLLUTION

The amount of pollutants entering the atmosphere is the largest factor influencing air pollution. It has been observed that although emissions into the atmosphere remain steady for long periods, large variations do occur from one day to the other. These variations are a consequence of changes in certain atmospheric conditions [35].

Figure 15, shows that the concentration of the metals are above the yearly average value (25.3 $\mu g/m^3$) during the first half of the year as compared to the below yearly average in the second half. An increase in concentration occurs from March to May, while a decrease occurs from August to November. The high concentration of Cu resulted in a larger total metal concentration for February.

Wind strength and Air stability are important atmospheric factors which affect the dispersion of pollutants, since they determine how rapid pollutants are diluted with the surrounding air once they have been emitted. A direct consequence of wind speed is that; higher wind speeds remove pollutants more rapidly away from the source, it also causes the air to be more turbulent thus diluting the pollutants with the surrounding air. This effect is clearly demonstrated in Figure 19, where the concentration increased from March to May with a corresponding decrease in the wind speed. The converse is true for increasing wind speeds where the concentration decreased from August to November (Figure 19).

When the air is unstable, the air currents carry smoke and exhaust fumes upwards were it is mixed with the cleaner air and dispersed by the winds above. The decrease in concentration with increasing temperature, from August to November (Figure 16) corresponds to the formation of an unstable air currents which result from a warmer surface temperature. The lower concentration of pollutants is reinforced by the increase in wind speed from August to November (Figure 19). The lower pollutant concentration for July as compared with that of August is due to the higher wind speed for July. A stable air condition results in Temperature Inversion, (cooler air layer is trapped by a warmer air layer above it) resulting in the suppression of vertical mixing and dilution of pollutants. In such instances the pollutant concentration remains high [35].

Rain, hail or combinations thereof are forms of precipitation. Precipitation result in pollutants being removed from the atmosphere before dispersion has taken place. The concentration of pollutants is at a maximum concentration during the initial stages of rainfall [31]. It is therefore expected that the concentration of the pollutants should be lower during months of higher rainfall. This effect is observed in July, August, September and October (Figure 18).

The temperature of the atmosphere depends on the rate at which energy from the sun reaches the earth. Temperature is not a constant and since it varies with factors such as height, latitude, season, time of day, etc. During the day the solar radiation is absorbed by the ground resulting in a warming of the earth's surface. At night the radiation of energy by the earth's surface will result in its cooling and result in an inversion layer. As a consequence pollutants accumulate during the night a few hundred meters above the ground. These pollutants are then carried to the ground in the morning as the earth's surface begins to warm; hence the pollution level will thus be increased at morning time and then decrease as the day becomes warmer [38]. Figure 16 indicates that the increase in concentration with decreasing temperature is a result of temperature inversion which had occurred during the day.

The relative humidity depends on the amount of water vapor required to saturate the air and is influenced by temperature. Generally a decrease in temperature increases the relative humidity, while an increase in temperature will result in a decrease in the relative humidity [35]. When the humidity is low the concentrations of suspended particulate pollutants increases; this accounts for the increase in pollutant concentration observed from March to May in Figure 17. High humidity, result in fog conditions, and can block solar heating of the ground surface and result in an unstable air flow (the life of inversion layers is increased) as consequence the concentration of the pollutants increases or remains high. Figure 17 also shows that the pollutant concentration decreased from September to November as the relative humidity decreased. Since the relative humidity is low, the wind speed and temperature high for December is observed, a pollutant concentration lower than November is expected, however this is not the case, thus implying that a stable air condition has occurred as a result of temperature inversion. It is apparent that temperature inversions occur mainly from December to May whereas stable air conditions occur from July to November.

CHAPTER 4

CONCLUSIONS

An analytical procedure was developed, using Differential Pulse Anodic Stripping Voltammetry technique as an analytical tool, for determining trace amounts of metal pollutants in the atmosphere. This has been successfully applied for the first time in the Republic of South Africa for airborne Copper, Lead and Zinc. These metals were emitted from motor vehicle emissions traversing past the sampling site.

The absence of a sediment after digestion and spurious peaks on the voltammograms implied that digestion was complete. Although the method of Standard Addition was used for quantitation, the use of a Calibration curve for quantitation is possible, and must be optimized, since good agreement between the two methods of quantitation was observed.

The variations in metal pollutants with the meteorological data has emphasized the influence of climatic factors such as wind speed, temperature and relative humidity in the cleansing of the atmosphere. Since the influence of climatic factors has been treated on a qualitative basis, no quantitative mathematical model could be generated. However, a quantitative evaluation is possible if the frequency of monitoring is increased over a longer period and at more than one monitoring site. The analysis time and sampling equipment for such a quantitative evaluation can become extremely costly and was not actively pursued in this instance.

APPENDIX

COPPER
CALIBRATION CURVE

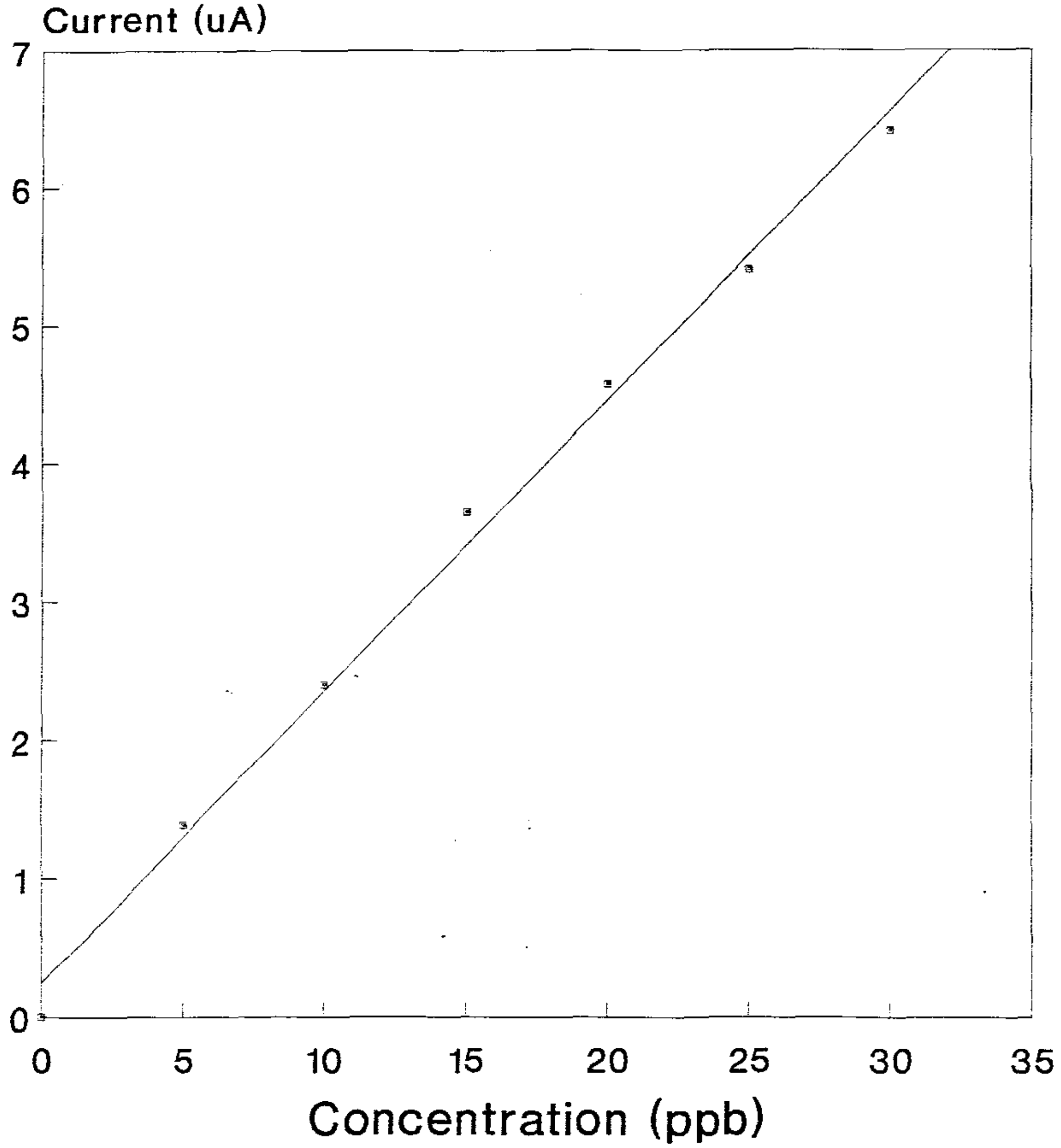

FIGURE 1

CADMIUM
CALIBRATION CURVE

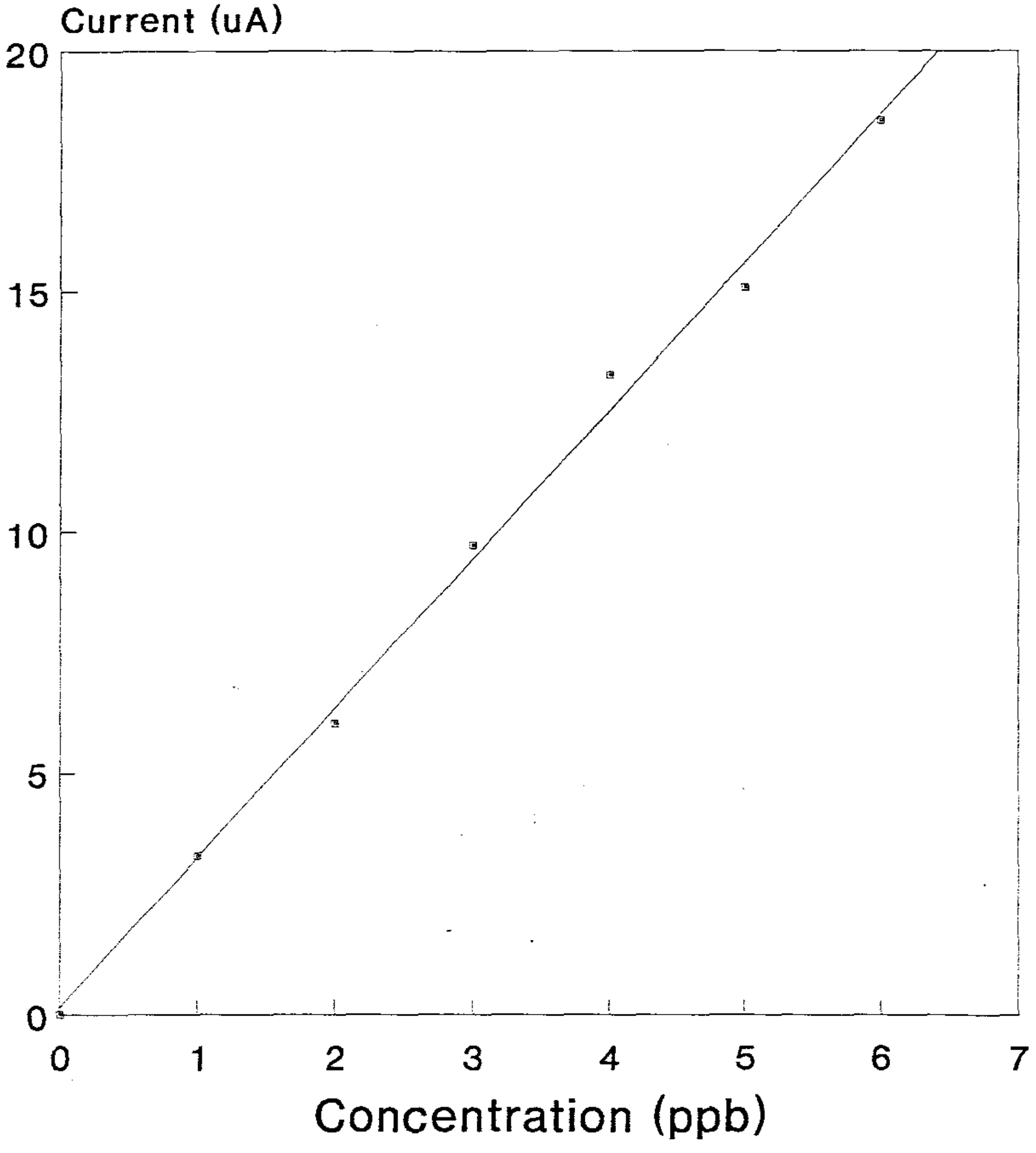

FIGURE 2

LEAD
CALIBRATION CURVE

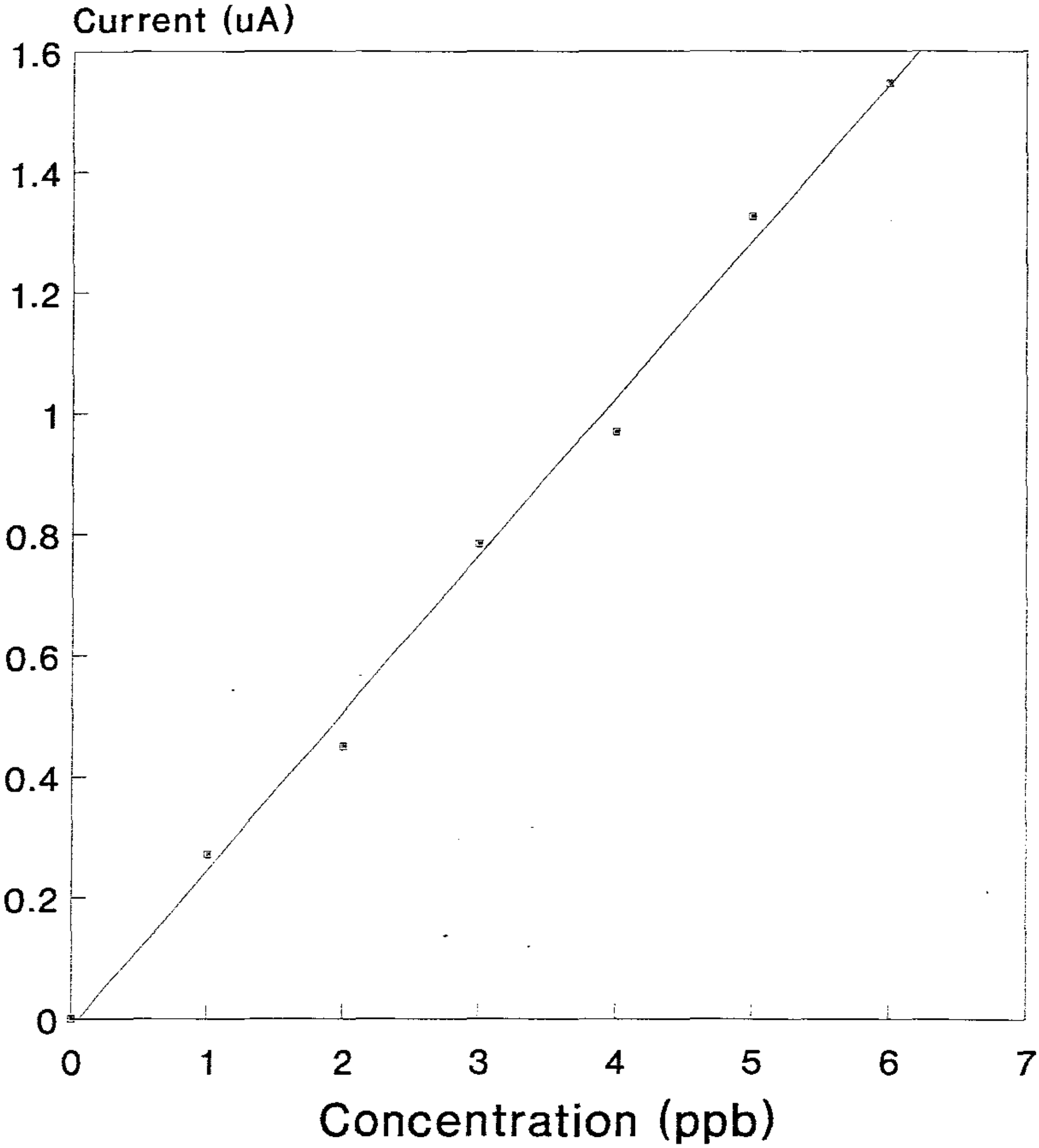

FIGURE 3

COPPER
STANDARD ADDITION METHOD

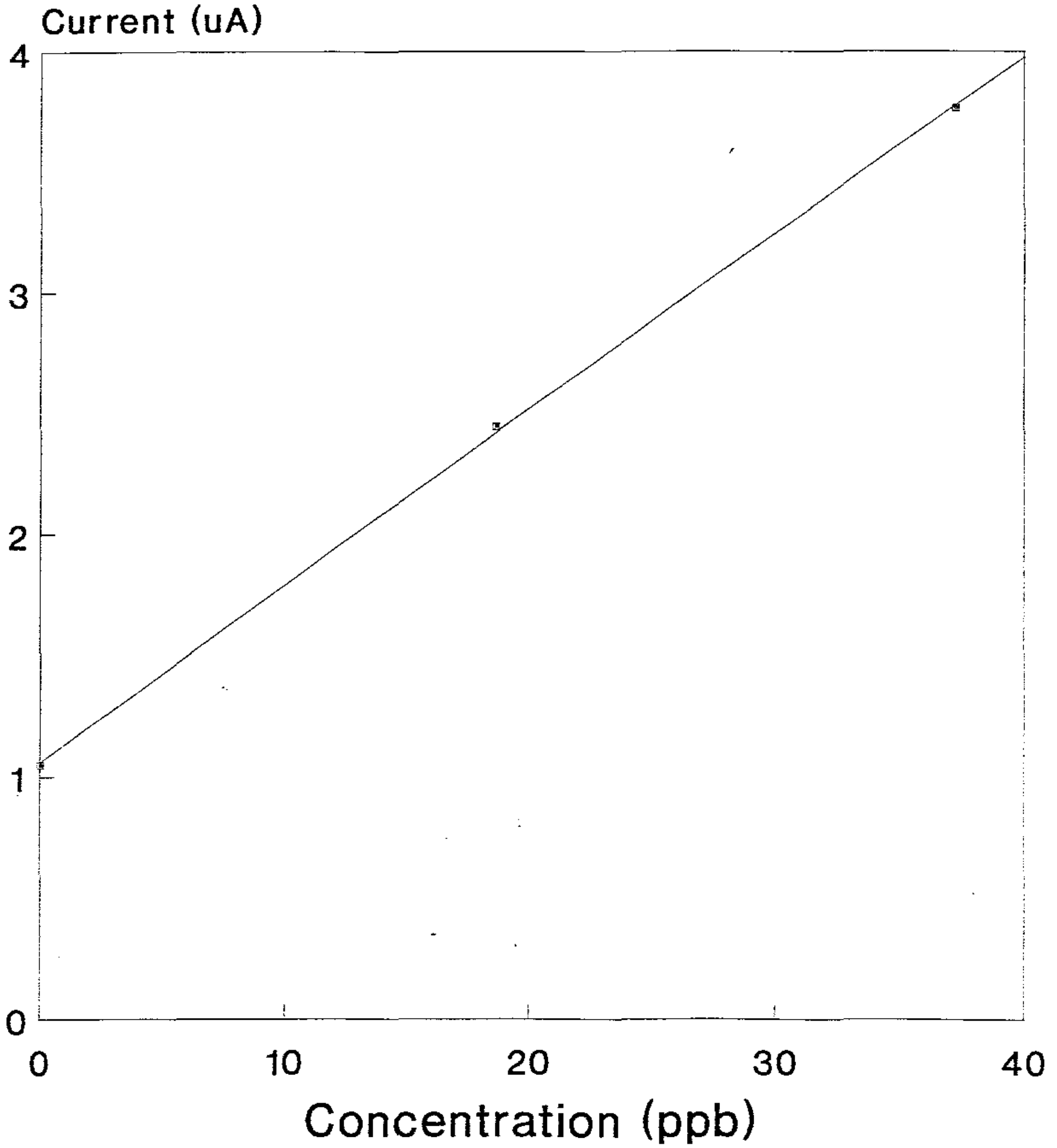

FIGURE 8

LEAD
STANDARD ADDITION METHOD

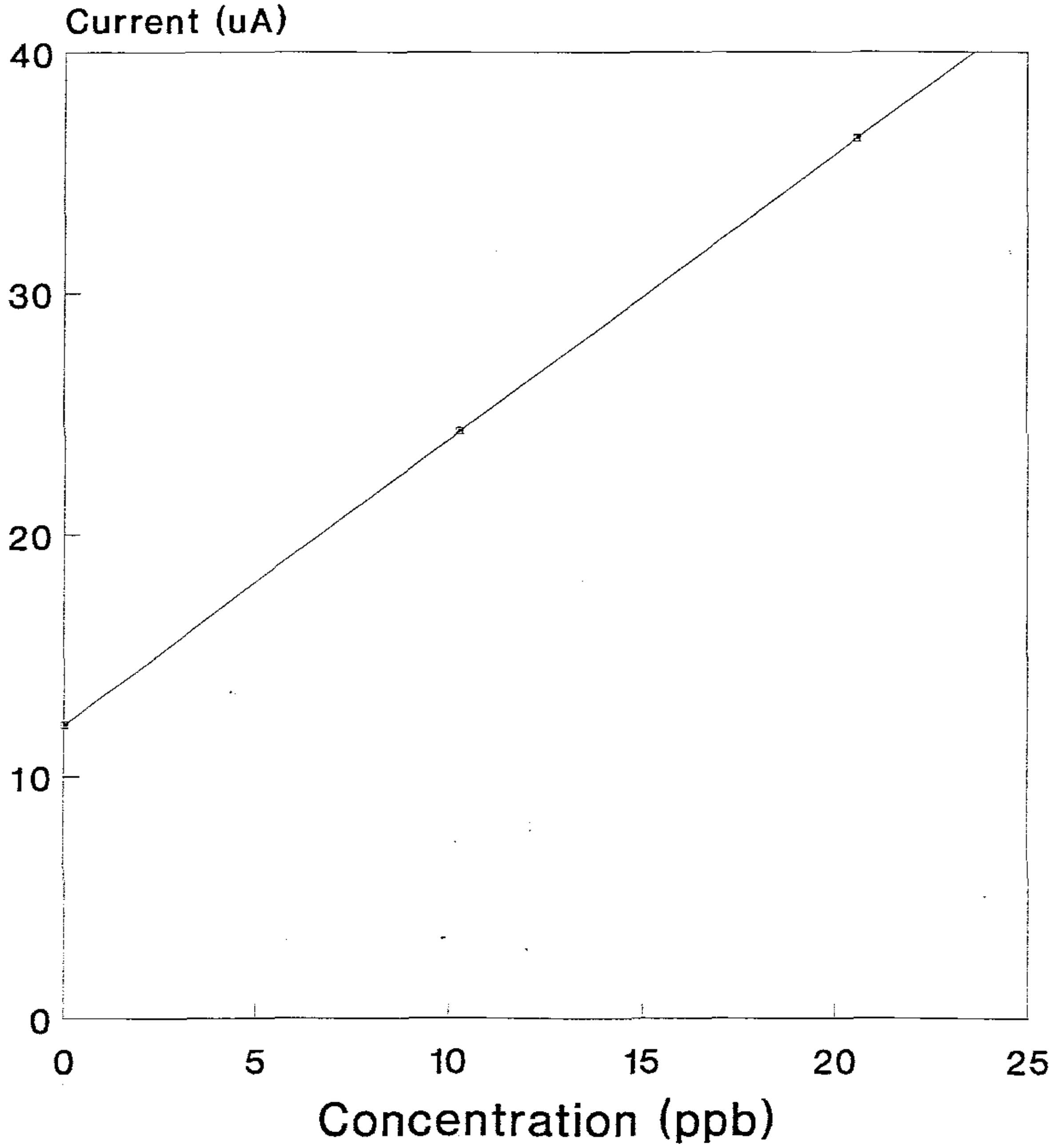

FIGURE 9

ZINC
STANDARD ADDITION METHOD

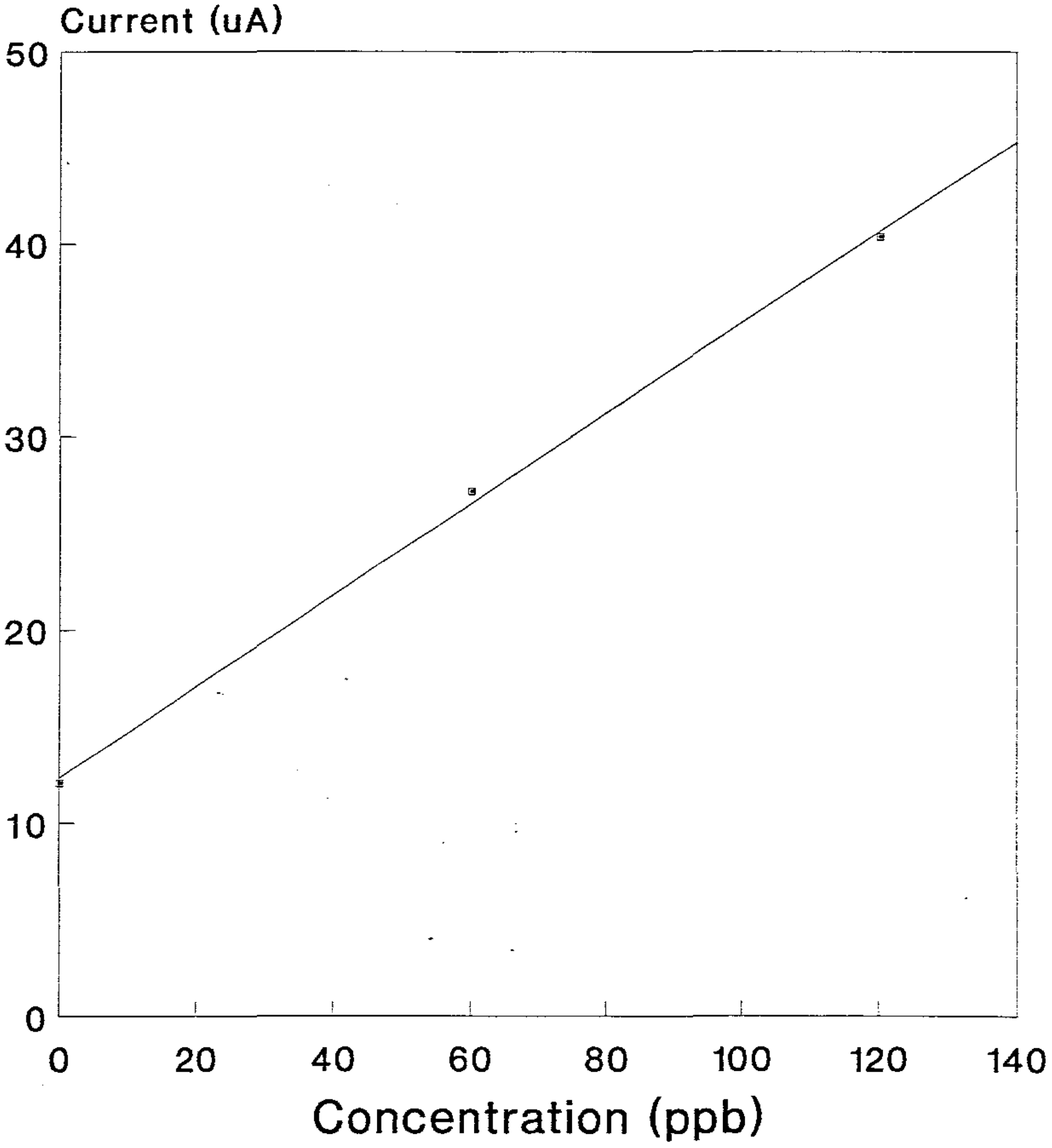

FIGURE 10

REGRESSION ANALYSIS DATA FOR STANDARD ADDITION CURVES

	Copper	**Lead**	**Zinc**
Slope	0.073	1.18	0.235
X - intercept	-14.05	-10.29	-52.45
Correlation Coefficient	0.999	1.00	0.999
Concentration (ppb)	14.05	10.29	52.45

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