ONTARIO PRECIPITATION CHEMISTRY AND HEAVY METAL SPECIATION

ONTARIO PRECIPITATION CHEMISTRY AND HEAVY METAL SPECIATION

By

DEAN STUART JEFFRIES, B.Sc.

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
October, 1975

DOCTOR OF PHILOSOPHY (1975) (Geochemistry) | McMASTER UNIVERSITY Hamilton, Ontario.

TITLE: Ontario Precipitation Chemistry and Heavy Metal Speciation

AUTHOR: Dean Stuart Jeffries, B.Sc., McMaster University

SUPERVISOR: Dr. James R. Kramer

NUMBER OF PAGES: ix, 125

ABSTRACT

Gross Ontario rain and snow chemistry and heavy metal speciation was determined on samples collected from a precipitation sampling network established in Hamilton and Northern Ontario. Relative to surface waters, precipitation is normally a low conductivity (mean value = 34 μmho/cm (25°)), low pH (4.3) system with elevated heavy metal (10 - 100 μg/l) and nutrient (50 - 100 μg/l P; 400 - 2000 μg/l N) concentrations. Anodic stripping voltammetry (ASV) was employed to determine "soluble" heavy metal speciation. ASV peak potential shifts and current measurements were used as criteria in making this determination. Unusual anodically shifted Cu peaks common to many precipitation samples suggested a Cu-colloid association. Duplication of polarographic behaviour observed for natural precipitation samples was obtained with synthetically prepared Fe-Mn colloids. In terms of "soluble" Cu speciation, Northern Ontario could be divided into two distinct regions; near Sudbury rain and snow contained aquo-Cu^{++} ion at elevated concentrations, while in the remainder of the province, precipitation contained colloidally associated copper. Zn, Cd, and Pb were generally present as the aquo-species. Rain-out of colloidally associated copper into the higher ionic strength environment of lakes will probably result in metal desorption and colloid flocculation. Copper would then be available as a biologically toxic species.

ACKNOWLEDGEMENTS

This thesis represents the tangible culmination of my Ph.D. studies at McMaster University. My Ph.D. study embodied not only the accomplishment and reporting of original research, but also a day-to-day learning experience which better prepared me for future scientific careers. In both regards, I owe an immeasurable debt to the following people:

Dr. James R. Kramer, who supervised my work and provided numerous occasions for the broadening of my scientific horizons. I trust we both have a sense of accomplishment and gain as a result of our association;

Dr. Werner Stumm, who supervised my work in Switzerland (December, 1973 - August, 1974) and arranged, in true Swiss tradition, to make my stay there as enjoyable as possible;

Drs. H. D. Grundy and Y. K. Chau, who, along with Dr. Kramer made an excellent Ph.D. committee;

Jill Gleed and Abdul Kabir, who have been primarily responsible for the practical aspects of acquiring the large precipitation chemistry data bank now in existence;

Pat Young, who typed this thesis with no complaint, despite my personal pressure. She has provided varied and unfailing secretarial service whenever I asked for it.

Finally, I must thank Wendy, who, more than anyone else, has influenced and encouraged me throughout my Ph.D. 'career' and to whom this thesis is dedicated.

TABLE OF CONTENTS

Page

CHAPTER III

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Air chemistry and its relationship with the rest of the environment has only come under considerable scrutiny in the last twenty years. Ignorance of the role played by the atmospheric system in influencing the geochemical and biological cycles which control the environment is slowly disappearing with more and more study. Man has been unable to exert a great enough perturbation on natural ecological cycles to cause much change until very recent times, but with the advent of the industrial revolution and the consequent exponential increase in technological capability, this fact is no longer true. At present, careful environmental planning and control is necessary to maintain the relatively delicate natural balances by which we all survive. In order to achieve this control, a comprehensive understanding of each of the components of the geochemical cycle is necessary.

This study was undertaken as part of an ongoing atmospheric research program with the goal of determining overall Ontario precipitation chemistry and factors affecting it, and the chemical form of heavy metals in precipitation.

The importance of an atmospheric pathway within the geochemical cycle is now recognized. Evaluation of the factors affecting this route (i.e., sources, transport mechanisms, chemistry, deposition processes, etc.)

is complicated by the as yet poorly understood inter-relationships among them. For example, simple turbulent mixing of atmospheric components may make determination of a specific source for a given material very difficult. It is, therefore, not surprising that research in this area still exists at such fundamental levels as determining overall chemical composition, investigating the physical and chemical processes governing composition and distribution, and studying input/output relationships. In comparison, research in marine science was at this level many years ago.

A thorough understanding of the chemical forms in which heavy metals exist in nature is necessary if accurate prediction of their environmental effects is desired. Determination of this chemical "speciation" has not received major attention until recently, however, due to the much higher proportion of research time and technological development directed towards analysis of the low level total component concentrations normally found in the environment. Species determination simply adds another dimension of complexity to an already complex situation. Nevertheless, this knowledge is ultimately necessary in order that a correct understanding may be developed of the role played by a given element in the biological and geochemical cycles controlling the environment.

The term "species" will be used here to refer to the form(s) in which an element exists in the aquatic phase. The definition of species also includes the possibility of particulate and/or colloidal association or dispersion.

Most analytical methods measure total amounts rather than determining components in specific chemical states. The information thus obtained is inappropriate for use in predicting the interactions that a particular component will undergo in the environment. Moreover, water quality standards based on total concentrations have a similar "built-in" insufficiency. For example, Table I illustrates the variation of lethal threshold concentrations of Cu, Zn, Pb and Cd in rainbow trout in fresh water as a function of total hardness. Although strictly speaking hardness is not a measure of carbonate/bicarbonate levels, it does normally mirror alkalinity values in natural water systems. It is immediately apparent that increases in Ca, Mg and CO_3^- concentrations result in increases in fish resistance to heavy metal lethality. The factor that does remain constant, however, is the concentration or relationship of the particular species or group of species which causes death in the fish. This concentration (a function of the remaining physical and chemical parameters of the system) is the most appropriate water quality standard. However, methods have not been readily available to determine either what species is critical or the lethal concentration. Hence, water quality criteria take the form of "total" metal concentrations.

The importance of a thorough understanding of heavy metal speciation in the aquatic environment cannot be over-estimated. With this information, accurate prediction of their possible reactions can be made. This fact has considerable toxicological importance. As discussed by Browning (1961), different metal species often exhibit substantially different metabolic and toxicological effects. For example, lead is inherently toxic to man

TABLE I LETHAL THRESHOLD CONCENTRATIONS OF SOLUBLE COPPER, ZINC, LEAD, AND CADMIUM IN RAINBOW TROUT IN FRESH WATER[1]

Total Hardness (mg/l $CaCO_3$)	Incipient LC50 (μg/l)[2]			
	Cu	Zn	Pb	Cd
10	30	490	770	39
15	41	610	860	68
20	52	720	930	102
25	62	820	1000	142
50	109	1210	1230	385
100	192	1810	--	1060
500	710	4500	--	11000
1000	1230	6700	--	30500

1. Adapted from "Guidelines for Water Quality Objectives and Standards", Inland Waters Branch, Environment Canada, Tech. Bull. No. 67, 1972.
2. The LC50, or the lethal threshold, is the concentration which causes death to half the animals studied for indefinitely long exposures. Valid for pH near neutral and summer temperatures.

in all its forms; however, methylated lead species attack the human organism by a very different biochemical pathway than do inorganic lead species. Nickel, which is generally considered non-toxic to man in almost all forms, has one highly carcinogenic species, i.e., the carbonyl. Copper in its elemental form is generally considered non-toxic, but as the acetate or sulphate, it is acutely toxic to humans. Copper sulphate is a traditionally used algaecide, with its toxic properties usually ascribed to the action of the Cu^{++} ion. It has been recently shown (Allen, 1974), however, that in most natural surface waters, particularly those classified as "hard" waters, copper is present as the carbonato-complex.

It is becoming increasingly clear that simple determination of total component concentration provides insufficient information to allow evaluation of its environmental impact. Osterberg (1974) has studied metal-protein interactions in the aquatic environment. Since all metals affect almost all life-forms through progressive metal-protein reactions, comprehension of these basic first order reactions is necessary before any subsequent or resulting toxicology may be understood. As Osterberg points out, experimental study of these reactions requires analytical methods which are species specific. Methods which involve the measurement of EMF may have this specificity and, in particular, ion selective electrodes and polarographic techniques are suitable.

With regard to Water Quality Standards, the inadequacy of the "total" component concentration analysis has been summarily noted as follows:

> "In almost every instance,.....(literature reported data for).....the essential element, with no description of the ionic form included. Therefore, it is difficult to relate the reported concentrations to health because toxicity is dependent upon the ionic, salt, or complex forms of the element."
>
> (U.S. Environmental Protection Agency, Water Quality Criteria Data Book, Vol. 2, p. 18)

Hence determination of "free" component concentrations and various complex species should be the ultimate aim of the researcher. The technological capability and chemical understanding necessary to achieve this goal are still in the developmental stage.

II. PRECIPITATION CHEMISTRY

II.1 Atmospheric Processes

Atmospheric components (particulates and gases) are transported and deposited by four natural processes; this applies to both man-made components (i.e., pollutants), as well as naturally occurring materials. First, dry-fall of relatively large particulates which have become airborne through the application of some "abnormal" force (i.e., stack emission, high wind, etc.). Dry fallout normally occurs reasonably near source, but is naturally dependent on a variety of other atmospheric conditions. Second, gaseous and fine particulate redistribution may occur via diffusion. Dispersion of stack plumes and long-distance transport of aerosols occur via this process, and are more dependent on other physical factors (atmospheric turbulence, windflow intensity and direction, thermal structures, etc.). Third, washout is the collection and deposition of atmospheric components by falling precipitation particles, i.e., and impaction process occurring below cloud base. Observed precipitation concentration of a given component is a function of the collection efficiency of the falling rain or snow particle, which is itself determined by several other factors. Finally, rainout or snowout is the inclusion of atmospheric components at the time of formation of the precipitation particles, that is, an "in-cloud" process. In some cases, aerosol particulates may act as precipitation nucleation centres. It is immediately apparent that observed precipitation chemistry is the result of several complex atmospheric interactions; nevertheless, it serves as an overall indicator of air quality and has been used on several occasions in this regard.

II.2 Previous Work

II.2.a Early Studies

First studies of air chemistry began in the late 1800's with the investigations of some trace substances in precipitation; similar work appeared sporadically during the next fifty to sixty years, commonly taken in relation to nutrient source studies in agricultural research (Crowther et al, 1911). During the late 1950's and early '60's, interest in this field heightened dramatically as numerous radioactive fallout studies were undertaken and the complex relationship between atmospheric and precipitation component concentrations were realized (Greenfield, 1957; Van Der Westhuizen, 1969; Moeken et al, 1963). The reported possibilities of extensive atmospheric transport, coupled with knowledge of significant photochemical and oxidation reactions taking place spurred the introduction of air chemistry studies from a total system point of view. The first major precipitation sampling program was developed by E. Eriksson in Scandanavia. Expansion of this network occurred until all of western Russia, central Europe and Britain were covered. Analyses usually performed were Na, Ca, Mg, Cl^-, $SO_4^=$, NO_3^-, NH_3 and specific conductivity.

II.2.b Atmospheric Chemistry and its Relationship to Precipitation Chemistry

Precipitation sampling is an indirect method of air quality monitoring which has found extensive use. Kortzeborn and Abraham (1970) have investigated precipitation scavenging of air particulates by the washout process. They have shown that scavenging efficiency and precipitation composition is a function of particulate size and rain-drop size, which is in itself governed by evaporation rates, drop coalescence, and rainfall intensity. A computational model for prediction of washout efficiency was developed.

Engelmann (1971) studied precipitation scavenging of SO_2 and developed the following washout relationship:

$$\frac{k}{X} = \frac{\rho n}{qE_2} + \frac{(1-n)\rho\alpha}{q} + \frac{H\Lambda}{R} \qquad (1)$$

where

k and X = the concentrations in rain and air, respectively;
ρ = density of water;
q = absolute humidity;
E_2 = efficiency of the cloud at removing water vapour as precipitation;
n = fraction of pollutant which nucleates and is scavenged;
α = a dimensionless reactivity factor for gases with water;
H = height of cloud base;
Λ = washout coefficient for the precipitation rate R.

The complexity of the problem is clearly evident from the number of other factors which must be considered when attempting scavenging and precipitation chemistry prediction.

Postma (1970) studied rain drop absorption of gases, and found that final precipitation concentrations were governed by gas solubility, drop size, and reaction rates once absorption had occurred.

It is evident from these studies that precipitation chemistry will provide a good, although indirect, indication of overall air quality. Cloud formation and subsequent precipitation fall is an efficient mechanism for cleansing the atmosphere of its particulate and gaseous impurities.

II.2.c Air Particulate Studies

Characterization of air particulates has been the subject of much research. These studies usually employ high volume filtration and collection of air particulates on a filter matt, followed by appropriate chemical analysis. In addition, cascade impactors have allowed sizing of the particulate samples and determination of those components which strongly correlate with one particular size range. As the relationship between particle size and precipitation scavenging efficiency is better understood, this sizing technique will find more and more application.

Lee et al (1969) studied the heavy metal size distribution of an urban aerosol (Cincinnati, Ohio) using the above methods. They found that Pb was consistently found in the smallest size fraction (sub-micron) while Fe, Cd, Cr, Mg and Cu were much more evenly distributed in the larger size fractions. Several studies of Pb in the atmosphere have concluded that automobile exhaust emission is its principal source. Strong correlation between roadway proximity and elevated ambient Pb levels has been confirmed by Yoshitaka et al (1970), Harrison et al (1971a) and Daines et al (1970). Harrison et al (1971b) used "Hi-Vol" particulate sampling in Northwest Indiana, along with neutron activation analysis of thirty trace elements. They were able to distinguish two separate groups; one which showed minor concentration variations throughout the sampling area (Na, K, Ti, Al, Sm, Eu) and the other, which showed marked variations indicative of important local sources (Cu, W, Cr, Zn, Sn, Ga, Br, Ag, Fe, Ce). Their results are supported by those of Morrow et al (1971) who, in addition, were able to find a strong correlation between Ca, Al, Si and Mg. The relative atmospheric abundances of these elements was in the same proportion as that found in the earth's crust; clearly wind-blown dust is the chief atmospheric source for these elements.

Finally, Kniep et al (1970), in their study of New York City air particulates, were able to distinguish a seasonal pattern for certain elements. Ni and V were found to be highest in the winter and were attributed to the increased heating oil combustion occurring at this time of year. Pb, Cu and Cd were found to directly correlate with temperature, although average windspeed was also important.

II.2.d Organics and the Atmosphere

A variety of techniques have been employed for the study of atmospheric organic compounds. Lao et al (1973) collected "Hi-Vol" samples and after soxhelet extration, determined the associated polycyclic aromatic hydrocarbons. They were able to identify over seventy different compounds.

The use of gas chromatography-mass spectroscopy has greatly increased the ability to identify components of complex organic mixtures. Grob and Grob (1971) used this technique to identify one hundred and eight different organic compounds in the air of Zurich, Switzerland. Benzaldehyde and several alkyl derivatives were among those compounds identified. Using much the same techniques, Altshuller et al (1971) studied the diurnal variation of atmospheric organics in the Los Angeles Basin. It was found that total organic content could be closely correlated with traffic intensity, and that 80% of all atmospheric hydrocarbons could be accounted for by ten species (ethane, ethylene, acetylene, n-butane, isopentane, propane, toluene, n-pentane, m-xylene and isobutane).

Total organic levels are much higher in urban areas and have been shown to primarily originate from fuel combustion processes (fuel oil, automobile emissions, etc.). In non-urban areas, overall levels are much lower and are commonly dominated by naturally occurring compounds (e.g., terpenes in coniferous wooded areas).

Finally, Sidle (1967) investigated the amino acids content in British precipitation. He found that their presence was a persistent and widespread phenomenon with glycine, valine, alanine, glutamic acid, aspartic acid and leucine positively identified. He failed, however, to indicate concentration levels.

II.2.e Precipitation Studies

Precipitation sampling has found extensive application, although sampling techniques have ranged from the very crude (funnel, sample bottle arrangement) to the very sophisticated (closed-top samplers which open during periods of precipitation and fractionate samples according to the amount collected).

Summer and Hitchon (1971) have investigated the source and budget of sulphate in central Alberta precipitation and concluded that rain is a much more effective scavenger than snow, and that in-cloud scavenging (rainout) accounts for most of the $SO_4^=$ observed in precipitation. This same generalized conclusion was obtained by Makhon'ko (1967) who, in addition, showed that aerosols are scavenged more than an order of magnitude more efficiently than gases. Further support for these observations is the work of Mrose (1966). He compared the concentrations of several parameters determined for precipitation and condensed fog-water. Since fog has an essentially infinite time span for aerosol and gaseous impurity scavenging (when compared to falling precipitation), it is not surprising that the fog had concentrations almost one order of magnitude higher.

Selenzneva (1972) considered the relationship of marine and continental constituents in precipitation in an attempt to define background concentrations for different geographical regions in the U.S.S.R. He concluded that over continental areas, background could only account for 30 - 40% of the total "contamination" observed. On a local scale, 60 - 70% could be attributed to nearby sources, while conversely, even in the most remote regions, 20 - 30% of precipitation contamination was of anthropogenic origin.

Oden (1971) and Likens _et al_ (1972) have discussed the problem of "acid rain", noting specifically the gradual decrease in the pH of Scandanavian lakes which has occurred in this century. Similar effects are present in many of the northern Ontario Shield lakes (i.e., not carbonate buffered), where decreased pH has resulted in the essential elimination of primary productivity and associated fisheries (Beamish and Harvey, 1972). This problem is caused by the deposition of atmospheric sulphate by precipitation; Likens suggests that 75% of sulphur in the air results from human activity. In contrast to this, in non-urban areas where oceanic winds prevail, and in very remote continental areas, rain pH approaches a value of 5.5, suggesting atmospheric CO_2 buffering.

In most cases, precipitation collection and analysis programs have been directed towards elucidation of major ion composition and have generally disregarded trace contaminants. The major exception to this was the NCAR study of 1966-67, reported by Lazrus et al (1970). In a national (U.S.A.) precipitation collection program, they were able to show that human activity constituted the primary source of Pb, Zn, Cu, Fe, Mn and Ni in rain and snow. In particular, Pb concentrations were found to correlate well (geographically) with gasoline consumption. This is in good agreement with the air particulate studies mentioned previously.

In all of these studies, heavy metals have been considered only from a total or soluble component aspect and never from a chemical character viewpoint. Determination of the chemical species of a given metal in precipitation is of great importance, since knowledge of this will have a direct influence on the expected environmental effects of the contaminant under consideration.

II.3 McMaster Precipitation Sampling Networks and Analytical Train

The McMaster precipitation study was initiated in 1970 as a portion of the thesis of N. Conroy (Conroy, 1971). The morphology and chemistry of twelve lakes near Sudbury was studied, and the failure to obtain a reasonable charge balance calculation using the "normal" major ionic composition lead to the assessment of atmospheric sulphate input. Since then, precipitation collection and analysis has been carried out in the Hamilton area (15 stations for approximately one year, 1972) and most comprehensively, in northern Ontario and the Sudbury region in particular, where a network of more than 30 stations is operative at present (Figure 1).

"Total" monthly samples, i.e., precipitation plus dry fall, have been collected and analyzed for 29 parameters (Table II) following the procedure flow scheme outlined in Figure 2. The sample collection device is the central "tube" type (as described by Kramer, 1973), and is surrounded by an alter shield which serves to enhance collection efficiency, particularly for snow. The central 4-foot high tube has a polyethylene liner which extends to its base, where it opens into a white polyethylene pail. The pail serves the dual purpose of sample collection vessel and, once sealed with a snap-on lid and placed in a special box, as shipping container as well. Removal and changing of sample buckets is facilitated by a sliding "trap-door" at the base of the tube. A container re-cycling scheme has been developed so that once all analyses are complete and after an acid-wash-deionized water rinse, the same bucket is sent back to the same station. Possible inter-station contamination is minimized in this way. Sample changing and shipping is conscientiously carried out by persons with easy access to the sampler. It may be noted that this sampling

Figure 1

Northern Ontario Precipitation Sampling Network

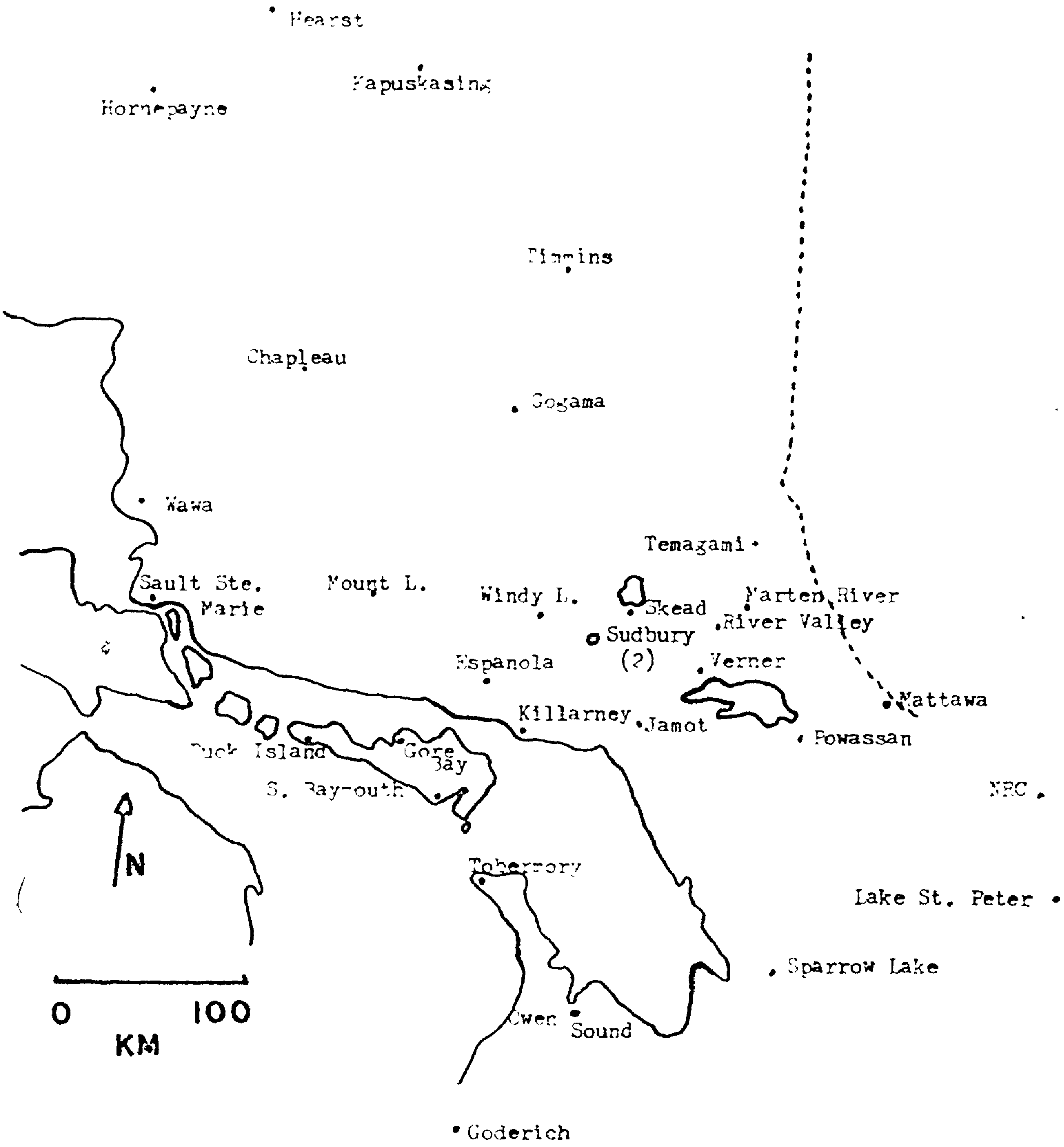


TABLE II

PARAMETERS MEASURED AT MONTHLY STATIONS

Parameter	Name	Method
CD F	Cadmium, filtered	Atomic Absorption
CD T	Cadmium, total	Atomic Absorption
CU F	Copper, filtered	Atomic Absorption
CU T	Copper, total	Atomic Absorption
FE F	Iron, filtered	Atomic Absorption
FE T	Iron, total	Atomic Absorption
Pb F	Lead, filtered	Atomic Absorption
PB T	Lead, total	Atomic Absorption
NI F	Nickel, filtered	Atomic Absorption
NI T	Nickel, total	Atomic Absorption
ZN F	Zinc, filtered	Atomic Absorption
ZN T	Zinc, total	Atomic Absorption
SPCON	Specific conductivity	Electrode
pH	pH	Glass Electrode
F	Fluoride	Electrode
CL	Chloride	Electrode
BR	Bromide	Electrode
SO4	Sulphate	Thorin titration
T PART	Total Particulate	Gravimetric
NA F	Sodium, filtered	Atomic Absorption
K F	Potassium, filtered	Atomic Absorption
MG F	Magnesium, filtered	Atomic Absorption
CA F	Calcium, filtered	Atomic Absorption
ALK F	Alkalinity, filtered	Electrode titration
P T F	Phosphorus, total filtered	Auto Analyzer
SIO2	Reactive silica	Auto Analyzer
NO3 F	Nitrate + Nitrate, filtered	Auto Analyzer
P T	Phosphorus, total	Auto Analyzer
NH3 R	Ammonia, reactive	Auto Analyser

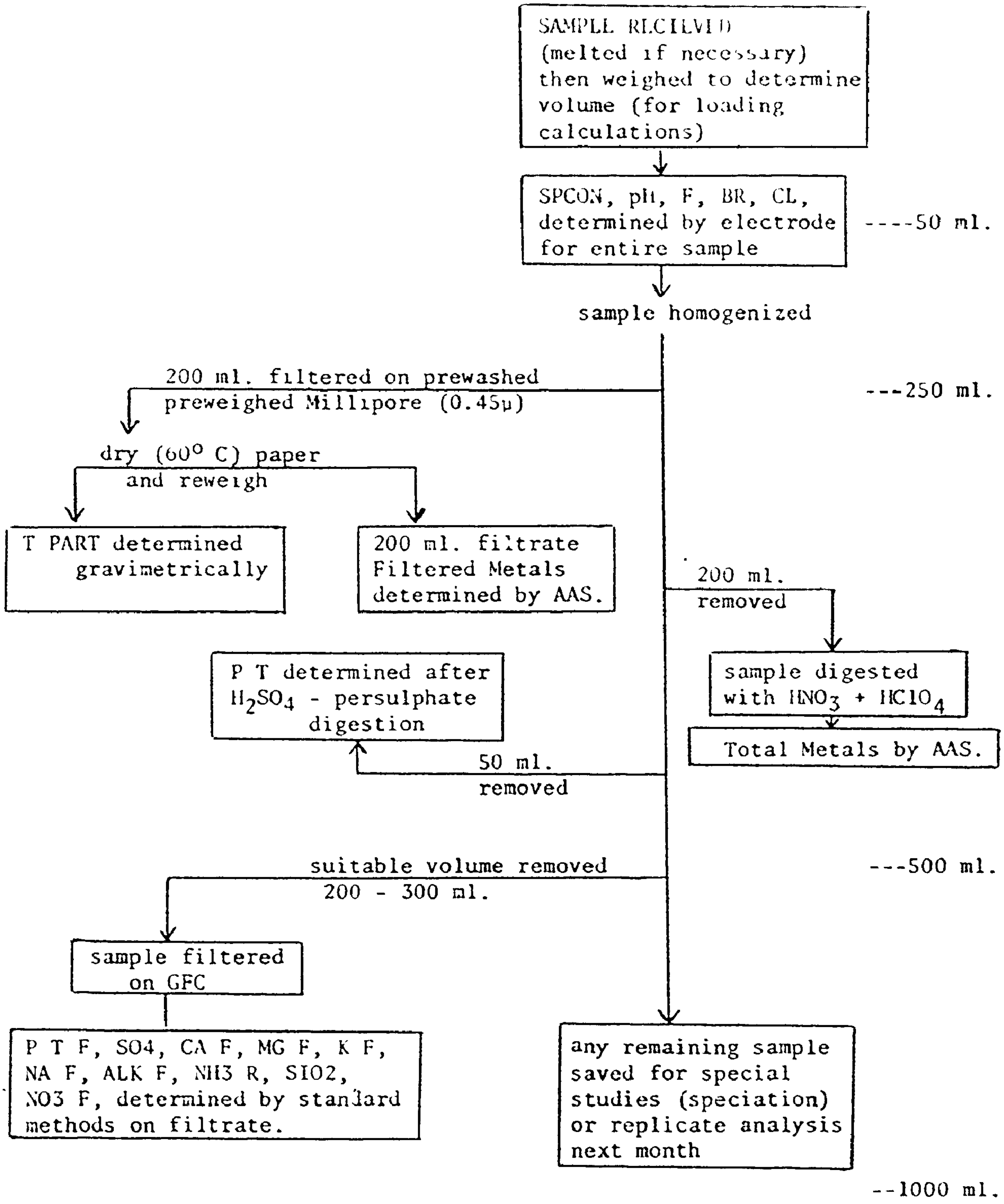


FIGURE 2 FLOW-DIAGRAM FOR SAMPLE ANALYSIS

method requires an absolute minimum of sample handling prior to arrival for analysis, a very desirable situation, since possible contamination is likewise minimized.

When all routine analyses are completed (see Appendix I for methods) and sufficient excess sample volume remains (as is commonly the case), various additional experiments and studies have been carried out. Among these is the polarographic determination of heavy metal speciation as given later.

The observed contamination of samples by insects, pine needles, etc., particularly during the summer months, coupled with the desire to separate the dry fall component from the precipitation analysis, has led to the development and recent deployment (1974) of three sophisticated "wet-only" sampling devices at Goderich, Duck Island and Wawa. This sampler type contains a precipitation sensor which, with the advent of a precipitation event, activates a "lid-opening" motor. The sensor, which operates in the same fashion as that of Lazrus et al (1970) and is completely described by Kramer (1975), allows collection of samples during precipitation events only, thus eliminating the dry fall component and substantial contamination. Sampling of individual events is also possible, so that determination of the subtle chemical differences related to the particular meteorological conditions associated with the event is now feasible.

A more complete description of the sampling network and several studies carried out in conjunction with it are given by Kramer (1973, 1975).

II.3 Precipitation Chemistry Results

Data summaries for the chemistry of Hamilton area rain and snow are given in Tables III and IV. Table III constitutes the concentration data as determined, while Table IV gives the corresponding "loading" parameters. Loading parameters give a value for the net atmospheric flux to the earth of a given constituent and are calculated using concentrations as determined above, plus sample volume and collection area. Units of g/cm^2/day are obtained and these values represent environmentally more significant figures than the pure concentrations which depend heavily on intensity and duration of precipitation, and also on the number of events in a given sampling period. Units for each parameter are indicated on the Tables.

Similar data summaries for the precipitation chemistry of the northern Ontario network are given in Tables V and VI. The time periods associated with each data set are Feb. - Dec., 1972 and June 1973 - Nov. 1974 for the Hamilton and northern networks respectively.

On each of the data summaries, note that parameter name, number of analyses (i.e., size), minimum, maximum, mean and standard deviation values are given for each parameter. Solubility has been operationally defined by 0.45μ membrane filtration and the parameters measured this way are designated with "F", for example, Cd-F. Total element analysis (i.e., Cd-T) was obtained after sample digestion. Particulate concentration may then be calculated by taking the

TABLE III

HAMILTON PRECIPITATION DATA SUMMARY[1]-- (CONCENTRATIONS)

Parameter	Size	Mean	Min.	Max.	Std. Dev.	Units
CD F	82	1.4	0.0	33.0	4.1	micro-gram/litre
CD T	83	4.7	0.0	120.0	15.8	micro-gram/litre
CU F	83	4.4	0.0	35.0	6.4	micro-gram/litre
CU T	82	30.4	0.0	285.0	43.7	micro-gram/litre
FE F	83	14.4	0.0	120.0	24.7	micro-gram/litre
FE T	82	877.7	0.0	4830.0	954.9	micro-gram/litre
PB F	79	5.3	0.0	35.0	8.0	micro-gram/litre
PB T	85	179.5	0.0	4540.0	501.0	micro-gram/litre
NI F	15	0.3	0.0	2.0	0.6	micro-gram/litre
NI T	14	7.9	0.0	23.0	6.7	micro-gram/litre
ZN F	83	97.1	0.0	270.0	66.4	micro-gram/litre
ZN T	82	557.0	4.0	4500.0	1002.4	micro-gram/litre
SPCON	71	59.	12.	210.	46.	micro-mho/cm (25)
pH	85	6.43	3.77	7.70	0.70	
F	85	311.	0.	1200.	312.	micro-gram/litre
CL	65	1161.	0.	7500.	1234.	micro-gram/litre
BR	85	38.	0.	118.	32.	micro-gram/litre
SO4	49	10.	3.	49.	8.	milli-gram/litre
T PART	82	.1173	.0000	1.0070	.2116	gram/litre

[1] Data coloected from February, 1972, to December, 1972.

TABLE IV

HAMILTON PRECIPITATION DATA SUMMARY[1] -- LOADINGS

Parameter	Size	Mean	Min.	Max.	Std. Dev.	Units
CD F	82	0.28	0.00	10.22	1.16	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
CD T	83	0.82	0.00	37.17	4.07	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
CU F	83	0.71	0.00	4.56	1.00	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
CU T	82	4.09	0.00	22.38	4.17	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
FE F	83	2.54	0.00	24.89	4.97	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
FE T	82	137.6	0.0	1185.7	191.9	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
PB F	79	0.96	0.00	9.77	1.87	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
PB T	85	19.6	0.0	169.4	26.4	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
NI F	15	0.03	0.00	0.26	0.07	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
NI T	14	1.00	0.00	2.87	0.82	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
ZN F	83	17.21	0.00	80.54	14.88	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
ZN T	82	87.4	0.3	1332.0	192.5	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
F	85	47.5	0.0	260.1	52.2	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
CL	65	208.7	0.0	1766.0	257.8	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
BR	85	6.1	0.0	27.8	5.6	$\text{gram/cm}^2\text{/day} \times 10^{-9}$
SO4	49	1.9	0.6	6.1	1.2	$\text{gram/cm}^2\text{/day} \times 10^{-6}$
T PART	82	0.0126	0.0000	0.0918	0.0185	$\text{gram/cm}^2\text{/day} \times 10^{-3}$

1. Data collected from February, 1972, to December, 1972.

TABLE V

NORTHERN ONTARIO PRECIPITATION DATA SUMMARY[1]-- CONCENTRATIONS

Parameter	Size	Mean	Min.	Max.	Std. Dev.	Units
CD F	425	0.9	< 0.0	12.9	1.1	micro-gram/litre
CD T	425	1.2	< 0.0	17.6	1.6	micro-gram/litre
CU F	425	26.1	< 0.1	1084.0	100.1	micro-gram/litre
CU T	426	42.4	< 0.5	1810.0	143.6	micro-gram/litre
FE F	409	36.	< 1.	896.	76.	micro-gram/litre
FE T	426	453.	< 1.	> 9999.	1002.	micro-gram/litre
PB F	425	17.	0.	142.	17.	micro-gram/litre
PB T	426	28.	< 1.	217.	25.	micro-gram/litre
NI F	425	13.	< 0.	464.	38.	micro-gram/litre
NI T	426	22.	< 0.	594.	62.	micro-gram/litre
ZN F	424	136.	< 1.	5279.	367.	micro-gram/litre
ZN T	425	174.	< 1.	5183.	403.	micro-gram/litre
SPCON	428	34.	1.	178.	25.	micro-mho/cm (25)
pH	428	4.26	7.86	3.47	4.28	
F	305	46.4	1.0	290.0	50.3	micro-gram/litre
CL	305	642.	10.	7400.	1080.	micro-gram/litre
BR	305	28.2	< 1.0	180.0	28.0	micro-gram/litre
SO4	418	4.2	< 0.0	23.3	3.3	milli-gram/litre
T PART	427	0.028	0.000	0.914	0.060	gram/litre
NA F	427	0.71	< 0.01	34.50	2.57	milli-gram/litre
K F	427	0.34	< 0.01	7.68	0.60	milli-gram/litre
MG F	351	0.3	0.0	2.2	0.3	milli-gram/litre
CA F	427	1.62	0.07	26.50	2.85	milli-gram/litre
ALK F	393	6.4	0.0	83.7	10.3	milli-gram/litre
P T F	426	91.	1.	3180.	245.	micro-gram/litre
SIO2	239	0.15	0.02	2.79	0.23	milli-gram/litre
NO3 F	238	0.93	0.01	82.00	5.29	milli-gram/litre
P T	426	188.	10.	3600.	329.	micro-gram/litre
NH3 R	49	0.37	< 0.00	2.66	0.37	milli-gram/litre

---

1. Data collected from June, 1973, to November, 1974.

TABLE VI

NORTHERN ONTARIO PRECIPITATION DATA SUMMARY[1] -- LOADINGS

Parameter	Size	Mean	Min.	Max.	Std. Dev.	Units
CD F	425	0.19	< 0.00	2.53	0.27	gram/cm^2/day x 10^{-9}
CD T	425	0.23	0.00	2.09	0.29	gram/cm^2/day x 10^{-9}
CU F	425	4.86	< 0.02	161.76	16.83	gram/cm^2/day x 10^{-9}
CU T	426	8.24	< 0.04	324.34	27.99	gram/cm^2/day x 10^{-9}
FE F	409	6.8	< 0.1	119.5	11.9	gram/cm^2/day x 10^{-9}
FE T	426	91.5	< 0.3	2752.4	219.7	gram/cm^2/day x 10^{-9}
PB F	425	3.8	0.0	27.0	4.3	gram/cm^2/day x 10^{-9}
PB T	426	5.8	< 0.1	50.1	5.9	gram/cm^2/day x 10^{-9}
NI F	425	2.4	< 0.0	47.5	6.3	gram/cm^2/day x 10^{-9}
NI T	426	4.6	< 0.0	188.0	14.7	gram/cm^2/day x 10^{-9}
ZN F	424	24.4	< 0.2	651.5	52.6	gram/cm^2/day x 10^{-9}
ZN T	425	32.2	< 0.1	867.4	69.7	gram/cm^2/day x 10^{-9}
F	305	10.1	< 0.1	74.2	12.1	gram/cm^2/day x 10^{-9}
CL	305	123.2	< 1.3	2035.3	207.3	gram/cm^2/day x 10^{-9}
BR	305	6.0	< 0.1	31.5	6.5	gram/cm^2/day x 10^{-9}
SO4	418	0.882	< 0.006	8.781	0.921	gram/cm^2/day x 10^{-6}
T PART	427	0.0053	0.0000	0.1068	0.0093	gram/cm^2/day x 10^{-3}
NA F	427	0.120	0.001	4.691	0.388	gram/cm^2/day x 10^{-6}
K F	427	0.067	0.002	2.248	0.138	gram/cm^2/day x 10^{-6}
MG F	351	0.06	0.00	0.43	0.07	gram/cm^2/day x 10^{-6}
CA F	427	0.324	0.003	5.239	0.616	gram/cm^2/day x 10^{-6}
ALK F	393	1.39	< 0.00	18.41	2.33	gram/cm^2/day x 10^{-6}
P T F	426	16.9	0.3	421.0	32.3	gram/cm^2/day x 10^{-9}
SIO2	239	0.026	0.002	0.170	0.028	gram/cm^2/day x 10^{-6}
NO3 F	238	0.145	0.000	7.246	0.467	gram/cm^2/day x 10^{-6}
P T	426	36.8	0.9	446.1	48.6	gram/cm^2/day x 10^{-9}
NH3 R	49	0.0953	< 0.0003	0.3521	0.0589	gram/cm^2/day x 10^{-6}

1. Data collected from June, 1973, to November, 1974.

difference between total and filtered values.

The data given here represents only a part of the total data collected during the past three years. Summaries of data by station are also available and are found in part in Kramer (1973) and Kramer (1975).

II.5 Discussion

When considering the massive quantity of data available, it is instructive to compare two sampling regions. Substantial differences in overall chemistry are, in most cases, easily explained. The Hamilton area network gave a comprehensive sampling of a highly industrialized region in close association with high urbanization. Steel production is the predominant industry, although substantial chemical and secondary industries related to steel are also present. The northern Ontario network on the other hand, provides a sampling of a large, reasonably unpopulated area with only point sources of industrial contamination, the massive mining and smelting operations at Sudbury being the most important.

As mentioned previously, the precipitation concentration of any given parameter is dependent on a number of meteorological factors; loading parameters provide a much sounder basis for comparison, since they at least take into consideration duration and intensity of rain/snow fall by incorporating sample volume. From Tables III and V it is immediately apparent that Hamilton precipitation is substantially less acidic than that of northern Ontario (Hamilton = 6.4, Northern Ontario = 4.3). This may be readily explained by considering the predominating geology of each region. The Hamilton area is situated on Silurian limestone and dolomite and thus a major fraction of re-entrained dust particulates in the area will be $CaCO_3$. Similarily, emissions of $CaCO_3$ and Fe-oxide from blast furnaces is to be expected (limestone used as flux in the smelting process). Thus precipitation in Hamilton should be reasonably carbonate-buffered and the observed higher pH is obtained. This is further substantiated by calcium analysis performed on samples collected at a later date and not included in Tables III and IV. Filtered calcium fell in the range 1.2 mg/l (pH = 4.07) to 20.2 mg/l (pH = 7.71) with a mean of approximately 4 mg/l. On the average, the Ca level in Hamilton is approximately three times that found in northern Ontario.

The geology of northern Ontario is dominated by the Shield, with gneisses, schists, and occasional sedimentary and/or glacial deposits. The availability of little natural $CaCO_3$ in the aerosol results in a poorly buffered system and this, coupled with the large H_2SO_4 emission from the Sudbury region, yields precipitation with consistently depressed pH which extends over a considerable area. The geochemical control of the master variable pH exerts a secondary influence on several other heavy metal parameters. Several observed differences between Hamilton and northern precipitation may be attributed to either source character or the difference in average pH. These differences are summarized in Table VII.

The inclusion of nutrient parameters in the northern Ontario data allows some evaluation of the relative importance of atmospheric input of these materials into surface waters. In general, precipitation phosphorus concentration is higher than that in most corresponding uncontaminated surface waters, and thereby represents a significant (though probably not predominating) source. Similarily, precipitation sulphate loading appears to be the primary source of this species for the Shield and Upper Great Lakes. The same statement may be made for nitrogen as well, where average rain and snow nitrate and ammonia concentrations are an order of magnitude greater than in surface waters. Atmospheric loading of silica, on the other hand, is an insignificant source.

Knowledge of "background" precipitation concentrations is of interest; however, it was clear from the data obtained from the geographically diverse northern Ontario network that sampling would have to be conducted considerably further away from any urban or industrial concentration in order to obtain meaningful results. In the summer of 1974 (June 25 - August 8), a sample was collected by Mr. B. Pratt on the Ram Plateau area west of the Mackenzie River and east of the Mackenzie Mountains in the Northwest Territories (Figure 3). Results of the analysis of the sample are given in Table VIII. All

TABLE VII

MAJOR HEAVY METAL DIFFERENCES BETWEEN HAMILTON AND NORTHERN ONTARIO PRECIPITATION

Parameter	Mean Loading ($g/cm^2/day$)		Reason & Comment
	Hamilton	N. Ontario	
FE T	137.6×10^{-9}	91.5×10^{-9}	-steel industry in Hamilton
PB T	19.6×10^{-9}	5.8×10^{-9}	-higher traffic density in Hamilton
ZN T	87.4×10^{-9}	32.2×10^{-9}	-higher industrial density in Hamilton
CU T	4.1×10^{-9}	8.2×10^{-9}	-mining and smelting industry at Sudbury
NI T	1.0×10^{-9}	4.6×10^{-9}	-mining and smelting industry at Sudbury
FE F	2.5×10^{-9}	6.8×10^{-9}	-higher filtered metals in N. Ontario is a function of increased solubility resulting from the lower average pH
PB F	1.0×10^{-9}	3.8×10^{-9}	
ZN F	17.2×10^{-9}	24.4×10^{-9}	

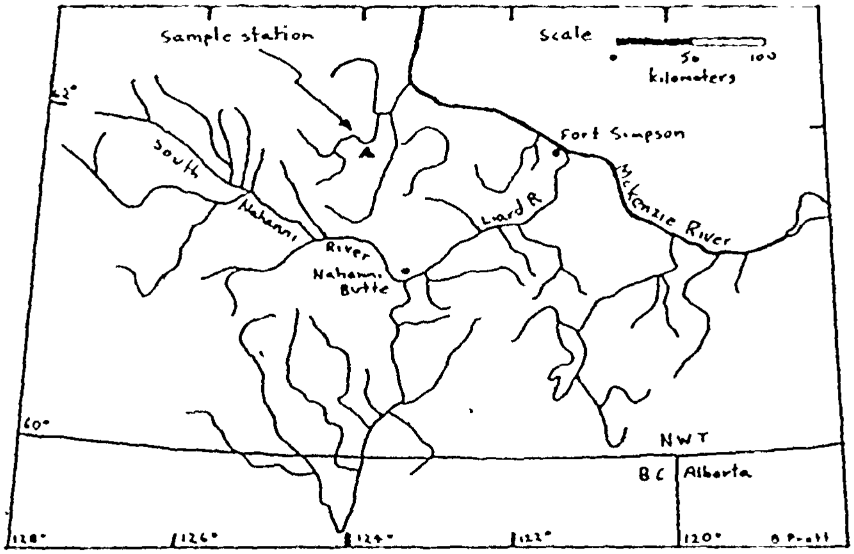


FIGURE 3 Location of Ram Plateau summer sample collected for background precipitation concentration levels.

TABLE VIII

RAM PLATEAU PRECIPITATION SAMPLE, JUNE 25 TO AUGUST 8, 1974.

Parameter	Concentration		Parameter	Concentration	
SPCON	14	mho/cm	pH	5.55	
CL	160	µg/l	F	77	µg/l
BR	17	µg/l	SO4	< 0.5	mg/l
CD T	0.2	µg/l	CD F	0.5	µg/l
CU T	1	µg/l	CU F	1	µg/l
FE T	31	µg/l	FE F	7	µg/l
PB T	1	µg/l	PB F	2	µg/l
NI T	0.3	µg/l	NI F	< 0.1	µg/l
ZN T	52	µg/l	ZN F	< 1	µg/l
NA F	0.02	mg/l	K F	0.15	mg/l
MG F	0.12	mg/l	CA F	0.4	mg/l
SIO2	0.012	mg/l	P T	139	µg/l
P T F	26	µg/l	NH3 R	0.012	mg/l
NO3 F	(high)				

parameters except phosphorus and nitrate are low, approaching analytical detection limits in most cases. Total iron and zinc values reflect geochemical abundance. Solubility of atmospheric CO_2 controls pH. The high phosphorus and nitrate values may be attributed to summertime biological recycling of these elements (insects, pollen, spores, etc.). This phenomenon has been found in all sampling areas, and in fact, leads to erroneously high average annual loadings of these elements. The net flux to the earth of P and N is best determined using only winter data when the above problem is minimal. The results obtained for this sample also compare favourably to those of a sample collected by Mr. R. Davie near Resolute, N.W.T. (Davie, R., 1974)

II.6 Additional Findings

Considerable effort has been directed towards the evaluation of the data by different members of the environmental geochemistry group at McMaster. A summary of the additional findings is briefly outlined below:

1) Concentrations of almost all parameters for northern Ontario precipitation are significantly greater than those of far north (i.e., background) samples. This may be attributed to singular or multiple local sources and/or inheritance from the continental U.S.A. (Kramer, 1975)
2) Geographic distribution plots (i.e., contours) of precipitation concentrations and loadings show the Sudbury industrial district as the primary source of contamination in northern Ontario for

most parameters measured. Contours normally take an elliptical form (long axis NE-SW), illustrating the influence of the predominating wind direction to the north-east. (Kramer, 1973, 1975)

3) Ambient concentration anomalies compared to U.S.A. levels have been investigated; in particular, ambient copper and iron concentrations are five times and nickel is twenty-five times. the U.S.A. mean. (Kramer, 1975)

4) Chemical budget considerations resulted in the observation that about 0.6% of total sulphur emitted, 100% of Fe and $SO_4^=$ (i.e., H_2SO_4), 70% of Ni and 40% of Cu emitted from Sudbury smelters are deposited in the area. (Scale = 100 Km) (Muller and Kramer, 1974)

5) Sulphur isotope studies (Kramer and Snyder, 1974) support the above observation, concluding that 0.4% of the SO_2 and 76% of the H_2SO_4 emitted can be accounted for in the 100 Km area.

6) While the activation of the 1200 ft. stack and employment of precipitators have effectively reduced total emissions, precipitation loadings for Ni have increased in size and geographic extent. This can only occur if Ni now being emitted is present in a finer particulate form and is thus carried farther before deposition.

7) Systematic seasonal variations in parameter concentration may be explained by various factors. Nutrient highs in summer are attributed to biological recycling ~~and perhaps~~ more efficient scavenging by rain than snow. This second factor accounts for elevated SO_4 and heavy metal values normally obtained

in the summer months, although re-entrainment of soils may be of some importance, particularly for iron. Scavenging efficiency is a complicated function of meteorological conditions (temperature, windspeed, mixing, etc.), particulate concentration, size, solubility, etc. (Kramer, 1975)

8) The Wawa iron ore mining and smelting operation has been shown to be a second major point source of iron in northern Ontario.

9) High concentrations of filtered heavy metals observed in northern Ontario may be primarily attributed to depressed pH; however, the case of filtered Fe is of particular interest. Predicted equilibrium soluble Fe concentrations (based on $Fe(OH)_3$ solubility calculations at the pH = 4.3 of northern precipitation) are approximately 20 μg/l. Filtered iron values are regularly in excess of this value, suggesting either Fe supersaturation, or else the presence of highly dispersed colloidal Fe which has passed through the 0.45 μ membrane filter.

II.7 Precipitation Chemistry - Environmental Perspective

An overall comparison of precipitation chemistry with that of "average" uncontaminated surface water is instructive. First, precipitation is a low pH, low conductivity, and low alkalinity system, completely unlike most highly productive lake waters. It is essentially an inorganic system, i.e., with little biological contamination excluding such airborne components as pollen and spores. Contamination of summer samples by insects, pine needles, etc., can initiate biological activity and under the conditions of high nitrogen, phosphorus and warm temperatures normally present, tremendous algal growth can occur. This has been observed on several occasions and leads to substantial problems in data evaluation. Several sampling procedure variations have been initiated to control this problem. Heavy metal concentrations in precipitation are usually at least one order of magnitude greater than in corresponding surface waters. This results from the depressed pH of the system, accompanied by the lack of clay and rock material for adsorption of such components. In limnological systems, heavy metal concentrations (usually 10μg/l or less) are buffered by a bottom sediment-water cation exchange mechanism. Particulate material settling through the water column adsorbs heavy metals and, after sedimentation, acts as a source of metals. As long as the gross chemistry (pH, Eh, alkalinity, ionic strength) of the lake does not change, an equilibrium is established between water and sediment which controls metal concentrations at their observed low levels.

The northern Shield lakes being situated in a silicate rock terrain, have very low carbonate buffering capacity, that is a very low alkalinity (and therefore low ionic strength). As a consequence, input of precipitation of such radically different chemistry has a very destructive effect. Decreasing the pH has resulted in decreasing primary productivity and associated fisheries. (Beamish and Harvey, 1972) Decreasing pH also upsets the equilibrium mentioned earlier; the cation exchange mechanism is pH-dependent following a reaction of the type given in Equation 2. Most common minerals have a pH(ZPC) in the range 4 - 5, so that pH depression towards this level causes increasing desorption of metals.

$$Me^{n+}\text{-}(X)_n + nH^+ \rightleftharpoons nH^+\text{-}(X) + Me^{n+}$$

metal adsorbed ⇌ metal desorbed

(X) = mineral surface

Thus biological activity is not only suppressed by conditions of high acidity, but also by metal toxicity as well. Loading of low pH precipitation is the primary cause of high acidity, high heavy metal concentrations and low productivity observed in many northern Ontario lakes.

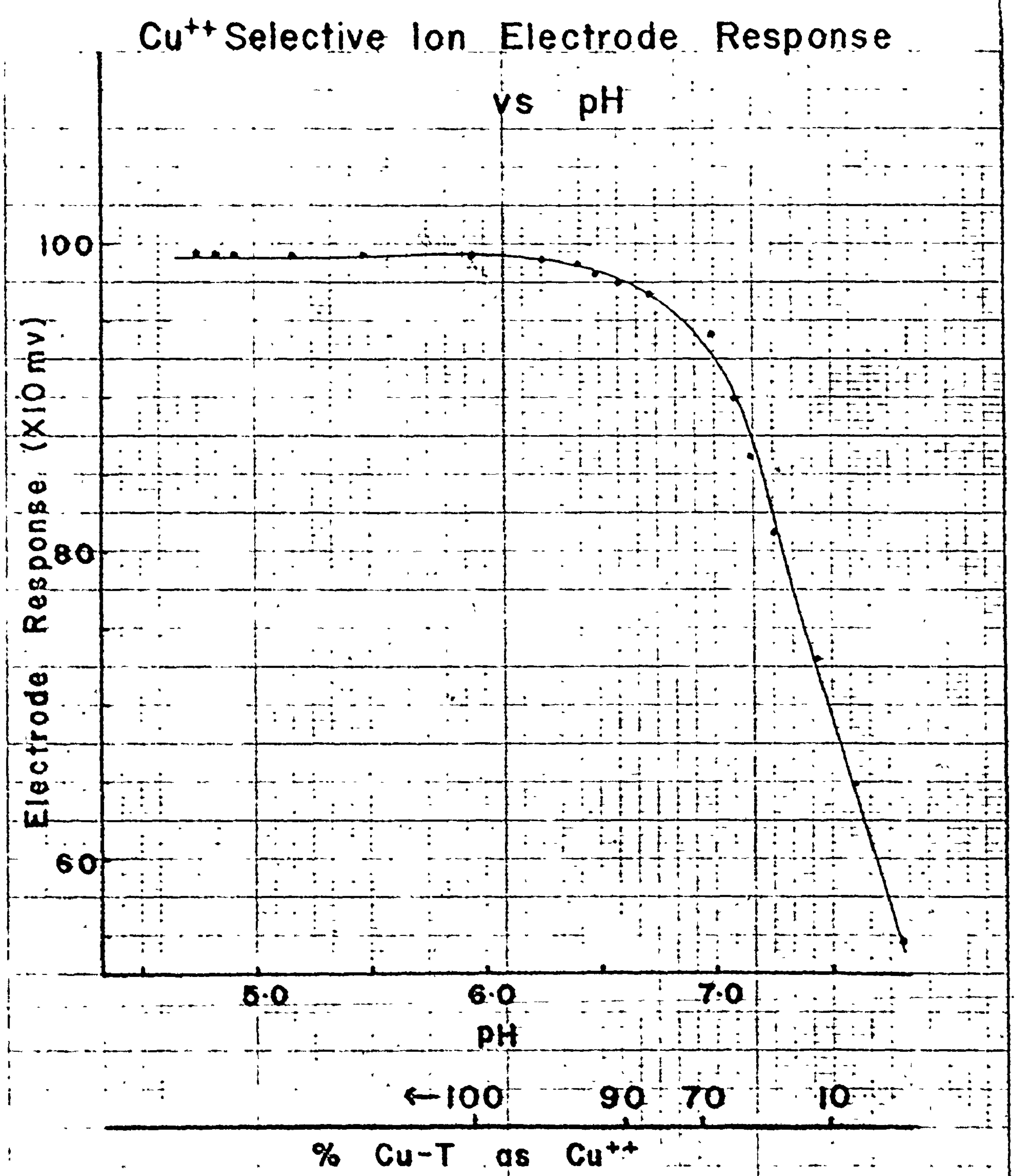
III. HEAVY METAL SPECIATION

III.1 Methods Available for Analysis

The traditional test for ionic copper is the diethyldithiocarbamate colorimetric procedure (Stickland and Parsons, 1967). Kamp-Nielsen (1972) has pointed out that this method consistently over-estimates the Cu^{++} species and recommends the use of either electrode or polarographic techniques.

Theoretically, selective ion electrodes are designed to respond to only one species of the element in question, normally the "free ion". However, in practice this may not be exactly true. Nevertheless, electrode response of the type shown in Figure 4 can be readily obtained for the cupric ion selective electrode. "Free" Cu measured by this method is a function of pH, with a rapid decrease in concentration obtained as pH is increased beyond 6.5, i.e., the result of Cu hydrolysis and electrode insensitivity to $Cu(OH)_x$ species. Stiff (1971) employed the cupric ion selective electrode coupled with various chemical methods to determine the copper speciation of polluted fresh water. Usefulness of electrodes is limited by an insufficient detection limit, however, which makes their application to uncontaminated samples impossible. As Stiff noted, systems with less than 50 μg/l total soluble Cu were inappropriate for electrode speciation. This necessary concentration level precludes speciation of precipitation from almost all localities except near the Sudbury region. It might also be noted that the selective cupric ion electrode is by far the most sensitive and dependable heavy metal electrode available today.

Figure 4


Cu++ Selective Ion Electrode Response
vs pH
100
80
60
Electrode Response (X10 mv)
5·0
6·0
7·0
pH
←100
90
70
10
% Cu-T as Cu++

Polarographic techniques monitor the progress of a reaction (oxidation or reduction) occurring at an electrode, and since specific species participate in the reaction (under known conditions), inferences with respect to component character may be drawn. Conventional dc polarography was one of the first analytical techniques capable of determinations at the 10^{-4} to 10^{-3} M concentration range. This is wholly insufficient for most natural samples; however, the development of several novel polarographic and voltammetric methods during the past few years now allows routine analysis in the 10^{-7} to 10^{-5} M range while still maintaining the signal dependence on chemical species. Even lower concentrations may be determined by anodic stripping techniques if sufficient care and the correct, analytical conditions are applied. A good summary description of these new methods is given by Flato (1972). A summary of species specific methods and reasons for rejection or acceptance is presented in Table IX. The most critical criterion is that the method must be capable of analysis of heavy metals at the concentrations which occur in northern Ontario precipitation, i.e., 0 - 50 μg/l ($\sim 10^{-6}$ M) in most cases.

III.2 Anodic Stripping Voltammetry

III.2.a Principle of Operation

Anodic stripping voltammetry (ASV) is a two-step electrochemical technique which derives its superior sensitivity (relative to dc polarography) from the use of an initial pre-concentration step. This step involves the electrolytic separation (reduction) of the metal of interest into or onto an electrode, a hanging Hg drop in this case, followed by a "stripping" step in which the metal is oxidized back into solution through

TABLE IX

SPECIES SELECTIVE METHODS

Method	Working Concentration Range	Reason for Acceptance or Rejection
1. Diethyldithiocarbamate colorimetric method	Variable	Rejected- (a) applicable only to Cu (b) reported to consistently over-estimate Cu^{++}
2. Selective ion electrodes (Cu, Pb, Cd, available)	$\sim 10^{-5}$ - 1 M	Rejected- (a) insufficient sensitivity (Cu electrode could find some use for near Sudbury precipitation)
3. Conventional Polarography	10^{-4} - 1 M	Rejected- (a) insufficient sensitivity
4. Anodic stripping voltammetry	10^{-7} - 10^{-2} M	Accepted- (a) sufficient sensitivity

the application of a linearly increasing potential. The current produced with the approach of the oxidation potential of the metal is measured along with the potential applied at any given instant and current versus potential polarogram obtained:

The preconcentration step (also known as the metal deposition or plating step) is performed at a known potential which is sufficiently more negative than the reduction potential of the species in question, so that deposition at the electrode is limited only by the rate of mass transport in solution. As mentioned by Allen (1974), species deposition follows the first order kinetic expression

$$M_t^o = M_i^{n^+} (1 - e^{-k_p t}) \tag{3}$$

where

M_t^o = amount of metal (M) deposited;
M_i^{n+} = amount of metal species (M^{n^+}) in solution;
k_p = deposition rate constant, and
t = deposition time.

The deposition rate constant may be expressed in terms of D = diffusion coefficient, A = the electrode surface area, V = volume of solution, and σ = effective thickness of the diffusion layer.

$$k_p = \frac{DA}{V\sigma} \tag{4}$$

This rate constant is only strictly applied to diffusion controlled metal deposition while, in practice, stirring of the solution normally occurs. Stirring insures a uniform and reproducible concentration gradient to the electrode, and also dramatically increases the deposition rate over that predicted by the above equation. Shain and Lewinson (1961) showed that a 500-fold concentration was obtained under stirred conditions, rather than the approximately 25-fold as predicted by the metal deposition equation. Analytical sensitivity is thus greatly increased by stirring. Reproducibility of stirring rate is essential, however, as is the size of the mercury drop electrode (i.e., constant electrode surface area), deposition time, and all factors affecting the diffusion coefficient, primarily temperature. Sample volume is less important. The critically important volume is that which is within the direct sphere of influence around the electrodes, although it should be noted that stirring will normally circulate the whole sample volume through this crucial portion of the reaction cell. Thus, as long as the overall sample volume is significantly larger than this critical volume, and only an insignificant amount of Mn_i^{n+} is removed from solution, then sample size is of lesser importance. For example, I have found that analysis of 25 and 50 ml samples yield essentially the same polarographic response where the cell used has an approximate critical volume of 10 ml. It is, nevertheless, normal procedure to maintain constant sample volumes to facilitate spiking of supporting electrolyte concentrates.

Variations in these parameters account for the greater part of observed analytical error, assuming no chemical interferences. With sufficient care, an error of less than ± 10% is possible for concentrations at the 10^{-7} M level (6.3 μg/l for Cu). Assigning an error estimate to each of the factors is impossible, although Siegerman and O'Dom (1972) suggest that the error in mercury drop reproduction is 3 - 4%.

As mentioned previously, the stripping step is accomplished through the initiation of a linearly increasing (i.e., anodic) potential scan at a fairly rapid rate (>20 mV/sec). Under these conditions, electrode radius is normally greater than the diffusion layer thickness, so that the stripping process may be considered as a semi-infinite diffusion process (Allen, 1974). Assuming these conditions, Barendrecht (1967) formulated the equation for the anodic stripping peak current (i_p) for a hanging mercury drop electrode (HMDE) system:

$$i_p = k' n^{3/2} Do^{1/2} r \nu^{1/2} tC \qquad (5)$$

where

k' = constant encorporating k_p of equation (4) and a mass transport constant;
Do = diffusion coefficient of the reduced metal in Hg;
n = number of electrons involved in the electrochemical reaction;
r = radius of the HMDE;
ν = potential scan rate;
t = deposition time; and
C = concentration of the metal in solution.

It is immediately apparent that polarographic response is a function of several variables other than just solution concentration and, of course, as mentioned previously, the object of most polarographic analytical methods is to consistently reproduce all these factors so that peak current variations may be related to species concentration. Analytical sensitivity may be increased by increasing t, ν, or r. HMDE radius is practically limited to that which the normal surface tension of Hg can maintain, and t is normally kept as short as possible (minutes) in the interests of determination speed. When a limited number of extremely high sensitivity analyses are required, however, deposition time may be increased to several hours. Sensitivities at the 10^{-9} and 10^{-10} M concentration levels have been reported using this technique. Increases in the scan rate (ν) may allow enhanced sensitivity; however, this is limited by a corresponding increase in the capacitance current (see below), which ultimately masks and, indeed, may overshadow any real change in the observed i_p.

The other important information provided by the polarogram is the peak potential. Under the same chemical conditions, the ASV peak potential (E_p) is related to the dc polarographic potential as follows:

$$E_p = E_{1/2} - \frac{1.1\ RT}{nF} \qquad (6)$$

where

$E_{1/2}$ = dc polarographic 1/2 wave potential;

R, T, n, F have their normal meanings.

Thus ASV peaks will be consistently $\frac{28}{n}$ mV (at 25°C) more cathodic than the corresponding polarographic 1/2-wave potentials.

The current measured by ASV is made up of two components: first, the current associated with the electrochemical reactions (Faradaic current), and secondly, the current required to form the electrical double layer at the mercury-solution interface, which is the background current obtained in the absence of electroactive species. This so-called capacitance or charging current (i_c) is what determines the detection limit of normal polarography and limits the scan rates applicable to ASV since i_c

varies directly with ν while i_p is a function of $\nu^{1/2}$ (equation (5)). Several methods have been employed to reduce or discriminate the effect of i_c, including phase-selective ac square wave voltammetry (Krause and Ramaley, 1969), and derivative techniques (Perone and Birk, 1965).

III.2.b Differential Pulse Anodic Stripping Voltammetry

Differential pulse anodic stripping voltammetry was used in my experiments. This technique employs the normal preconcentration step but a differential pulse voltammetry wave-form is used instead of the usual linear anodic potential ramp of ASV. This wave-form minimizes i_c contributions to the recorded signal as well as allowing signal processing for the removal of extraneous noise. This combination also yields a 1-2 order of magnitude increase in sensitivity (Siegerman and O'Dom, 1972).

The differential pulse voltammetry wave-form consists of a slowly increasing linear potential ramp with superimposed fixed height voltage pulses (Figure 5). The charging and Faradaic currents produced by the application of a potential pulse decay to an equilibrium value with time; however, the charging current decays much more quickly, so that measurement of the current towards the end of the pulse duration yields a current value which primarily reflects the desired Faradaic contribution. The PAR Model 174 polarographic analyzer used employs a pulse duration of 56.7 milliseconds; the first forty msec are used to allow i_c (i.e., background current) to decay to a negligible value whereupon the last 16.7 msec are used to measure the Faradaic current. Measurement of the Faradaic current just before and just at the end of the pulse period, and recorder display of the difference between these two values yields a peak-shaped read-out from which i_p and E_p may be accurately determined.

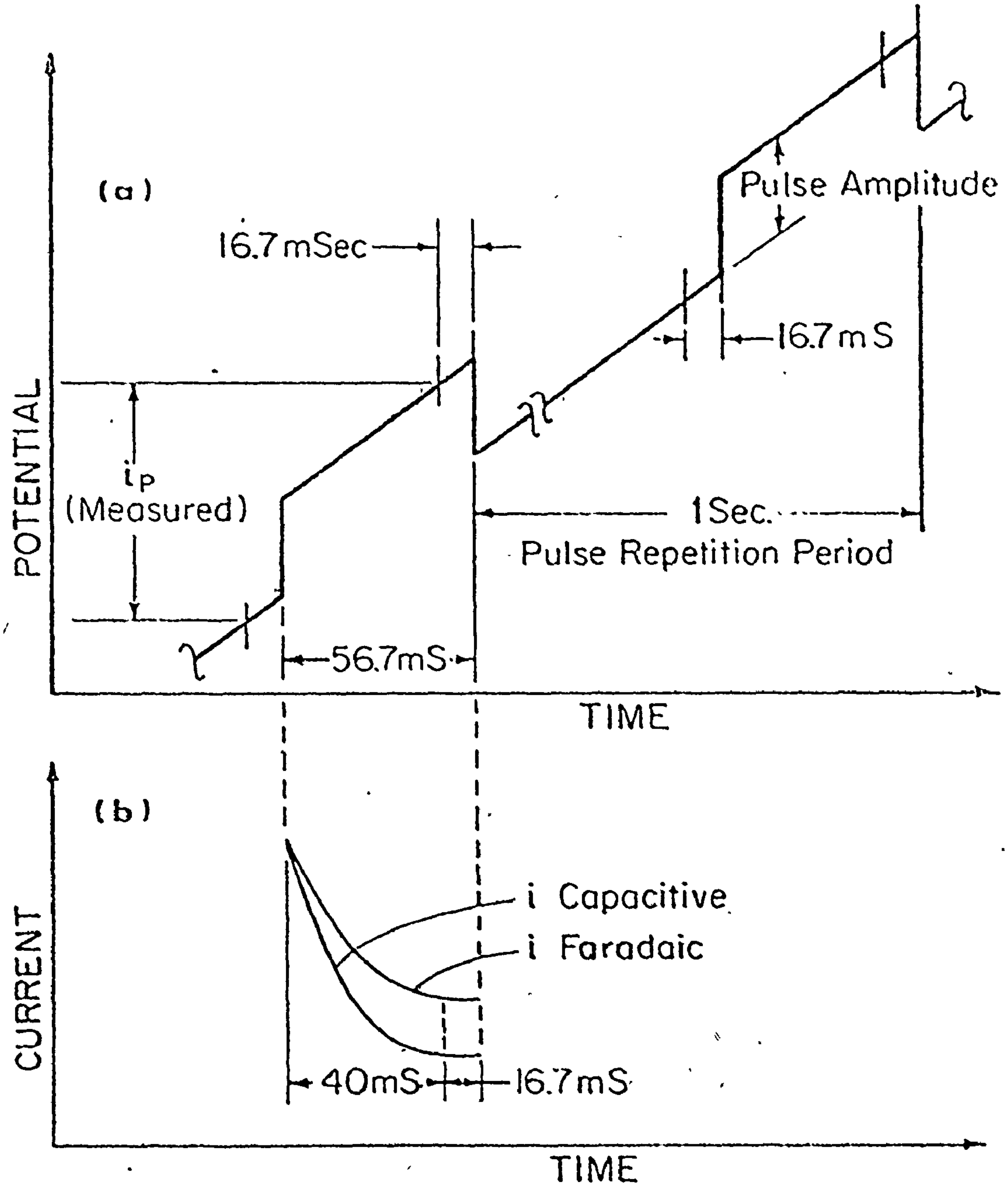


Figure 5 Differential Pulse Voltammetry Waveform.

(a) Excitation waveform

(b) Resulting current-time behavior

It may be noted that polarograms obtained using the HMDE are not completely symmetrical. This is the result of diffusion of metal from the interior of the drop and consequently higher background currents experienced after E_p than before. As would be expected, the MCGE suffers much less from this phenomenon since it has a much smaller mass of mercury from a metal diffusion point of view.

III.3 Theoretical Considerations

The general theory of anodic stripping voltammetry has been presented by Barendrecht (1967). As mentioned previously, the most important elements of ASV response are the peak current (i_p in μA), which is normally discussed in terms of peak height, and the peak potential (E_p in mV). The theoretical equation for i_p has been given earlier (equation (5)), while it was noted that E_p bears a direct relationship (equation (6)) with the normal polarographic half-wave potential, $E_{1/2}$.

Kolthoff and Lingane (1952) give the equation for $E_{1/2}$:

$$E_{1/2} = -\frac{RT}{nF} \ln \frac{f_a k_s}{f_s k_a} \qquad (7)$$

where

R, T, n, F have their normal meanings;

f_a, f_s = activity coefficients of the ion being studied in the Hg amalgam and in solution, respectively;

= a constant

$= E_a^o + \frac{RT}{nF} \ln a_{Hg}$

(E_a^o = standard potential of amalgam

a_{Hg} = activity of Hg in the amalgam), and

k_s, k_a = proportionality constants related to all the terms of the Ilkovic equation, except the solution concentration of the species under study, i.e., $k_s = 607\, nD_s^{1/2}\, m^{2/3}\, t^{1/6}$ at 25°C.

(D_s = diffusion coefficient of the ion in solution,
m = Hg flow rate,
t = drop time).

With reference to my experiments, one important point should be noted from equation (7). The activity coefficients are functions of ionic strength of the solution and, hence, as this parameter is altered, shifts in $E_{1/2}$ and therefore E_p should be observed. This is indeed the case. With increased ionic strength, E_p shifted to more negative potentials. The importance of understanding this phenomenon lies in the realization that it should not be confused with E_p shifts caused by complexation or by some other factor.

The half-wave potential of complex species was presented by Koryta (1962) for diffusion controlled processes:

$$E_{1/2} = (E_{1/2})_M - \frac{RT}{nF} \ln \sum_{i=0}^{n} \prod_{j=0}^{i} k_j [X]^i \qquad (8)$$

where

$(E_{1/2})_M$ = half-wave potential of the "free" metal ion as defined by equation (7);
z = nominal coordination number;
[X] = concentration of complex-forming agent present in sufficient excess;

k_j - consecutive stability constants defined by the equations

a) $k_j = \frac{[MX_j]}{[MX_{j-1}][X]}$, $j > 0$

b) $k_o = 1$.

From equation (8), it is immediately apparent that the presence of any complex forming agent results in a shift of $E_{1/2}$ (and hence E_p) to a more negative potential. The dependence of the magnitude of this shift on the complex stability constant allows calculation of the constant when all other factors are known, a method successfully employed by several authors as noted later.

In terms of ASV, the peak potential shift may be considered the result of ion stabilization by the presence of the complexing agent. After preconcentration, the metal of interest in the HMDE as an amalgam is re-oxidized back into solution by the application of a steadily increasing potential. The presence of a complex forming agent which serves to stabilize the metal ion in solution results in less energy being required to bring about re-oxidation. This fact is manifested in a peak (i.e., oxidation potential) shift to a more negative value. E_p may be shifted to more positive potentials if a second metal more strongly bound to the complexing agent is introduced; this fact has also been exploited in the determination of stability constants of added metal complexes.

There are four possible reasons for the occurrance of E_p shifts to less negative potentials than that corresponding to $(E_{1/2})_M$. First, the presence of a complexing agent which would stabilize the existence of a lower oxidation state of the metal would lead to a positively shifted E_p. Kolthoff and Lingane (1952) note that this phenomenon has been observed for the Cu^{++}-NH_3 system, in which low level NH_3 concentrations ($<5 \times 10^{-4}$M) result in positive shifts of $E_{1/2}$, principally due to the smaller dissociation constant of the $Cu(NH_3)_2^{+}$ complex than those of the $Cu(NH_3)_2^{++}$ and $Cu(NH_3)^{++}$ complexes. These are the major ammonical complexes which exist at this NH_3 level. (Based on von Stackelberg, M. and von Freyhold, H., Z. Electrochem. 46, 120 (1940).)

Second, kinetic rather than diffusion rate control of the electrode reaction may result in positive potential shifts. Koryta (1962) showed that polarographic potential shifts caused by this factor are related by the following equation:

$$(E_{1/2})_{kin} = (E_{1/2})_{dif} + \frac{RT}{nF} \text{lin} \frac{i_d}{i_l} \qquad (9)$$

where

$(E_{1/2})_{kin}$ and $(E_{1/2})_{dif}$ = half-wave potentials of the kinetically and diffusion-controlled cases, respectively;

i_d = limiting current of the hypothetical diffusion controlled situation (Ilkovic equation)

i_l = limiting current of the kinetically controlled case.

Clearly, only shifts to less negative potentials can occur.

Third, formation of intermetallic compounds in the mercury drop amalgam may cause peak potential shifts to less positive values. This phenomenon has been studied at length by Kozlovsky and Zebreva (1972) who point out that the polarographic half-wave potential of an intermetallic compound is normally somewhere between the half-wave potentials of the pure metals involved. Thus, if chemical conditions in solution are such as to promote the formation of a copper, mercury (and perhaps some other metal) intermetallic compound, E_p would be expected to shift to a more positive position relative to the E_p of the pure Cu case.

Finally, the ubiquitous "other" possibility: the problems caused by adsorption are well known and have plagued polarographers from the very beginning. Unfortunately, quantification of the effects of adsorption are impossible since adsorption of anionic, cationic, uncharged, electrochemically reactive and non-reacting species, either singly or in various combinations serve to provide all types of unusual polarographic behaviour. Reilley and Stumm (1962) have given a good discussion of electrode reaction inhibition by the presence of surface active species.

In summary, peak potential shifts obtained with ASV may be caused by one or more of the reasons outlined in Table X.

III.4 Previous Work

The chemical state of trace metals in natural H_2O systems has been the subject of several studies, although in almost all cases, the idyllic goal of a complete species by species description has proved impossible to achieve. This is only to be expected, given the immense complexity of the problem and the present stage of technological and educational development. Nevertheless, important information with regard to the existence of some metal-ligand species, associated stability constants, and research methodology is now available.

TABLE [illegible]

PEAK POTENTIAL SHIFTS AND ASV

Situation	Nature of Shift (relative to standard "free" metal E_p)	Comment
1. Change in ionic strength of solution analyzed.	Cathodic (see comment)	Cathodic shifts occur when ionic strength is increased, usually by addition of extra supporting electrolyte.
2. Presence of a complex forming species.	Cathodic	Magnitude of shift dependent on (a) concentration of comple forming species (b) magnitude of the stabil constant of the complex species.
3. In the presence of a complex species, introduction of another metal which forms a more stable complex.	Cathodic	E_p is cathodic relative to the standard "free" metal E_p, however it is anodic to the E_p obtained in 2. above.
4. Presence of a complex species capable of stabilizing a lower oxidation state of the metal.	Anodic	Magnitude of shift dependent on (a) concentrations (b) magnitude of the stability constant.
5. Electrode reaction kinetically controlled (rather than diffusion controlled)	Anodic	
6. Formation of inter-metallic compounds in the Hg drop amalgam	Anodic (usually)	E_p of inter-metallic compound falls between the E_p's of the pure metals involved.
7. "Poisoning" of the electrode and consequent reaction inhibition by surface active agents.	Variable	Reaction inhibition usually results in anodic E_p shifts.

III.4.a With Selective Ion Electrodes

Stiff (1971) proposed a scheme for differentiating copper into six chemical states (particulate, ionic, cyanide complexed, humic acid complexed, HCO_3-CO_3 complexed, and amino acid-polypeptide complexed) through various chemical separation methods and the use of the cupric selective ion electrode for ionic copper determination. Significantly, this procedure was only applied to studies of grossly polluted fresh water and would not be applicable to non-contaminated systems. As in almost all studies, "solubility" is defined by 0.45μ membrane filtration although the possibility of passing highly dispersed colloids is noted but not dealt with further. The chemistry of cadmium in natural waters has been studied by Gardiner (1974) using a selective ion electrode and a metal addition procedure to bring concentration within its detection capability. He found most cadmium present in the ionic form.

III.4.b With ASV

Most other authors have employed the superior sensitivity of ASV in an effort to directly determine speciation of uncontaminated aqueous systems. Matson (1968) used ASV with the Hg coated graphite electrode (MCGE) in suggesting a set of diagnostic tests which might be used to discriminate between "free" metal ions, labile organic complexes, and non-labile complexes with naturally occurring chelating substances. The presence or absence of double stripping peaks, peak potential shifts, peak shape changes, and alterations in plating rates, coupled with extensive theoretical considerations, were the criteria used in making species assessment. This seemingly simple method was studied by Hume and Carter (1972) who point out the problems involved in using the MCGE; for example, the production of double peaks at will simply by altering the electrode preparation conditions. From this standpoint, use of the HMDE is recommended, even though it is substantially less sensitive; it suffers a much smaller chance of surface poisoning since a new Hg drop is formed for each subsequent analysis. Secondly, the presence of any surface active agents in a sample may have substantial and usually unknown effects on the electrode reaction. "It is very difficult to distinguish between the effects of reaction and adsorption which, in fact, may be occurring simultaneously." (Hume and Carter, 1972.)

Barsdate and Matson (1966) used ASV to study the association of metals with organic substances in Alaskan lakes. They conclude that substantial organic association of Pb, Cu and Co exists in these lakes (organic substances of molecular weight >7000) and, in fact, a stoichiometric excess of a strong complexing agent was found in one lake which would alter metal cycling, oxidation-reduction, adsorption, co-precipitation, etc, processes. A crude calculation of the corresponding stability constant gave $K \approx 10^{24}$.

Systematic peak shifts to slightly more negative potentials for other lake samples were interpreted as the result of the presence of relatively weak complexes. Correlation between excess of strong complexing material and highly coloured (i.e., humic-rich) lakes was noted.

III.4.c Complexing Capacity Determinations

In an effort to quantify metal binding ligands in water, Allen et al (1970) presented a method using a complexometric titration with copper as the titrant; this procedure was employed by Bender et al (1970) to evaluate the complexing agents in secondary sewage. Chau et al (1974) have developed a method for the determination of total and excess "complexing capacity" of lake waters, expressed in terms of μmole of Cu equivalent. I have used this method to determine complexing capacities of several lakes in the Sudbury-Temagami, Ontario region. It should be noted that a complexing capacity measured (as above) by the ASV determination of the labile metal in Cu spiked samples is, in fact, a minimum value since the presence of weak and labile complexes yield anomalously high "free" Cu values. The complexing capacity thus obtained is best thought of in terms of the available strong complexing agents plus those which form kinetically inert complexes relative to the time span of the ASV analysis. This "definition" must follow from the definition of "lability" as operationally imposed through the use of ASV (Barsdate <u>et al</u>, 1974); that is, labile metals as determined by ASV are those which exist in a form which allows their ready reduction and reoxidation. Metals which are strongly bound within a complex are not readily reduced, and those which are present in kinetically inert forms will not react fast enough to be significantly detected by ASV. The concept of "lability" in relationship to ASV has been clearly summarized by Guy <u>et al</u> (1975). Chau and Lum-Shue-Chan (1974) have discussed at length the determination of labile and strongly bound metals (Zn, Cd, Cu, Pb).

III.4.d Metal Speciation Studies

Stumm and Bilinski (1973) and Allen (1974) have investigated speciation by ASV in natural waters and report that the predominant species in the pH range 6 - 9 is $PbCO_3^o$. Below this pH, "free" lead ions predominate. Allen has also found that carbonate is most important in determining the speciation of Cu, while Zn primarily exists as hydroxy complexes in the pH range mentioned previously (i.e., the pH of most natural lake, river, and ocean waters). It may also be noted that the Zn, Pb and Cu species discussed here are all "labile" complexes; that is, analysis of the metals by ASV yields appropriate though shifted stripping peaks. Hence, although these metals are complexed, they would not be included in a complexing capacity determination made as above.

III.4.e Stability Constant Determinations

Metal speciation has been taken one step further by the determination of stability constants of the metal-ligand species investigated by ASV. Polarographic determination of stability constants is an excellent technique due to its simplicity. By holding all other factors constant, stability constants may be directly calculated by substituting measured peak potential shifts (obtained as a function of ligand concentration) into equation 8. Allen (1974) reported $\log_{10}\beta$ values of 6.2 and 5.9 for the $PbCO_3^o$ and $CuCO_3^o$ metal-ligand systems, while Stumm and Bilinski (1973) obtained a value of 6.4 for $PbCO_3^o$. Bradford (1973) investigated the $Zn(OH)_2^o$

species and reported $\log_{10}\beta = 9.9$. In all cases, these results agreed very well with previously published values determined by other methods. Shuman and Woodward (1973) have proposed a generalized scheme for determining stability constants by using a complexometric titration, and monitoring labile metal with ASV.

III.5 Experimental

A Princeton Applied Research Corporation Model 174 Polarographic Analyzer with HMDE (PAR Model 9323), saturated calomel reference electrode (0.35M sodium acetate-acetic buffer salt bridge), and platinum wire counter electrode was used throughout. Polarographic response was recorded on a Houston Instrument Omnigraphic Model 2200-3-3 XY recorder.

Precipitation samples were processed in the following way:

1) 300-500 ml of sample were filtered through 0.45 μ Millipore membrane, directly into a nitric acid washed, deionized water rinsed storage flask.

2) A 25 ml subsample was placed in the polarographic cell assembly (PAR Model 9300 cell top and Model 9301 cell bottom) and 0.200 ml of sodium acetate-acetic acid buffer added as supporting electrolyte, giving an overall acetate concentration of 0.032M. Addition of this reagent also served to buffer the pH at 6.0 ± 0.1 for all samples of initial pH within the range 4.0 to 8.0. (See Appendix 2 for details of reagent preparation and/or purification.)

3) When "total" filtered Cu was required, 0.5 ml of 1:1 a HNO_3-$HClO_4$ mixture was added and the sample digested to dryness before redissolution in deionized water and transfer to the polarographic cell.

4) The sample was then stirred (Lab-Line Instruments, Inc.) and deoxygenated by bubbling of water-saturated pre-purified nitrogen for 10 minutes.

5) After diverting the N_2 gas flow over the solution surface, a five unit mercury drop (surface area = 2.6 mm^2) was extruded from the HMDE and plating carried out for three minutes (2 1/2 minutes stirred, 1/2 minute quiescent) using the following instrument settings:

Operating Mode = Differential Pulse
Drop Time = 1 sec (pulse rate)
Output Offset = OFF
Low Pass Filter = OFF
Display Direction = Negative
Pulse Modulation Amplitude = 25 mV
Potential Scan: Rate = 2 mV/sec
Direction = Positive
Range = 1.5 V
Intial Potential: Indicator = Negative
Coarse Adj = 0. volts
Fine Adj = 200 mV

Reproducibility stirring rates were maintained from sample to sample and all times were strictly controlled through the use of a stop watch.

6) At the end of the plating period, the differential pulse scan was initiated and continued until the mercury oxidation peak was encountered as indicated by an off-scale recorder response at a potential greater than +200 mV.

7) Depending on sample copper concentration, instrument sensitivity settings were placed at one of 5, 10, 20 or 50μA full scale.

8) When Zn, Pb, and Cu were determined simultaneously, plating was carried out at a potential of -1.200V; all other instrument settings remained the same.

9) DPASV determinations at pH = 0.7 - 0.8 were carried out after the intial analysis (pH = 6) by adding 0.600 ml HNO_3 to the cell, followed by thorough mixing and further deoxygenation (2 minutes). The large buffering capacity of the acetate supporting electrolyte system made the addition of this large quantity of acid necessary. The resultant substantial increase in solution ionic strength caused a shift in E_p to a more negative potential which was independent of acetate concentration as would be expected, since, at this pH, all acetate will be in the acid form and unable to associate with Cu and cause the large negative E_p shifts observed.

10) Experimants involving the separation of highly colloidal phases employed the use of an International Ultracentrifuge with A-237 fixed angle rotor. Centrifuging was done at room temperature and 49,000 rpm corresponding to 100,000 to 200,000 G force, depending on the position within the 30 ml sample vial. Once centrifuging was complete, 25 ml was pipetted immediately from the vial in order to minimize partial

redispersion of sedimented colloidal material.

11) Synthetic colloids were obtained by preparing solutions of known Cu, Fe, Mn, Si and Al content and increasing the pH with dilute NaOH to 9.5. After equilibration for 15 minutes, pH was decreased through the addition of dilute HNO_3 to a value in the range 6 - 7.

12) Complexing capacities of precipitation samples and some lake waters from the Sudbury area were obtained using the method of Chau et al (1974).

III.6 Results and Discussion

III.6.a Typical Polarogram Description and Interpretation

Typical polarograms for "pure" laboratory prepared solutions are given in Figure 6; well-formed peaks with constant E_p ($\approx$+4 ± 2 mV) and i_p directly proportional to copper concentration are obtained. The cathodic peak shift of the acidified sample (#4) is attributed to the increase in solution ionic strength with the addition of 0.6 ml HNO_3. Reproducibility of this E_p is more difficult (± 10 mV) than for the pH = 6 situation due to the difficulty of reproducible addition of concentrated nitric acid. A small peak more anodic than the main Cu peak (+120 - 130 mV) is commonly but not always obtained for calibration polarograms of this type. This phenomenon is attributed to a contaminant (probably surface active) in the deionized water supply, since it is present in the blank determination as well. Finally, its never-failing disappearance on the addition of acid should be noted.

FIGURE 6 DPASV Polarogram - Calibration

Polarogram 1 - Cu blank, pH = 6

Polarogram 2 - 0.8 μM Cu, pH = 6

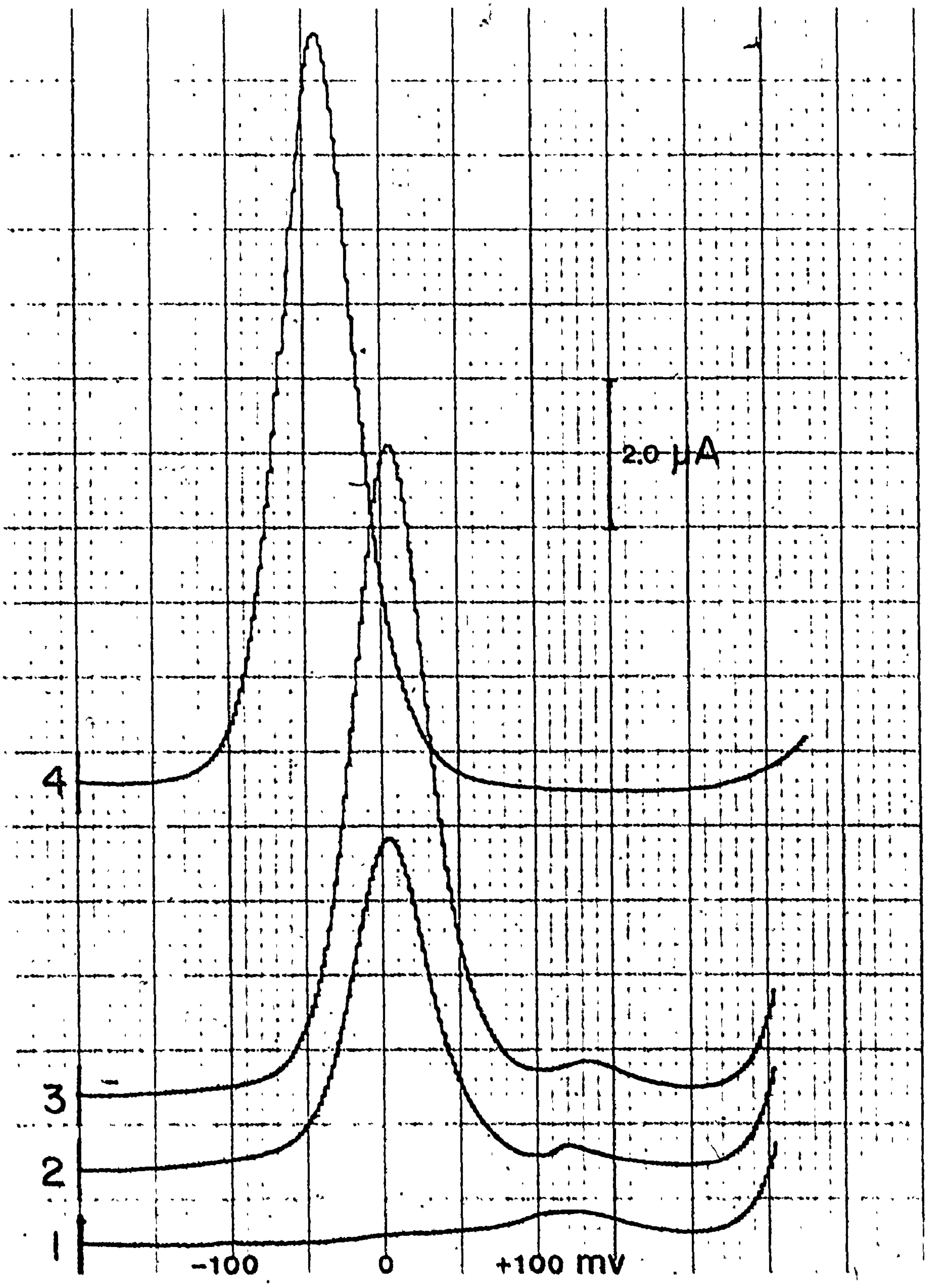
Polarogram 3 - 1.6 μM Cu, pH = 6

Polarogram 4 - 1.6 μM Cu, pH = 0.7

(0.6 ml HNO_3 added to 3)

Figure 6

DPASV Polarogram — Calibration



As mentioned previously, peak potential shifts and current changes of real samples may be used in the interpretation of metal speciation. Presence of "free" ion aquo complex will yield an E_p the same as that of the calibration polarograms, while complexation results in cathodic E_p shifts and sometimes decreases in i_p. Anodic E_p shifts must be attributed to one of the factors previously discussed.

Figures 7 - 9 (polarogram #1) present typical polarograms obtained for precipitation samples. Northern Ontario precipitation may be divided into two major region subgroups; first, the region immediately adjacent to Sudbury, where industrial activity plays a major role in determining precipitation chemistry. Low pH (3.7 - 4.4), high sulphate (1.0 - 12 mg/l), and total heavy metals, particularly Cu (50 - 450μg/l), Ni (30 - 300μg/l), and Fe (300 - 2400μg/l) are normally observed. The remainder of the province outside this predominating chemical influence constitutes the second region. For the most part, relatively higher pH (4.0 - 7.8), and low sulphate (0.3 - 6.0 mg/l), and low total metals (Cu: 0.5 - 150μg/l; Ni: 0 - 100μg/l; Fe: 10 - 1000μg/l) are observed. This is an overall simplification of course; local effects either on a one-time or continuous basis may play a substantial role in determining precipitation chemistry at a given station and must always be accounted for if possible. The ability to distinguish two principle regions (near to and far from Sudbury) is simply the consequence of the geographical log-normal

FIGURE 7 - DPASV Polarogram, Skead - Feb. 8 - Mar. 3, 1975

Polarogram 1 - Labile Cu, pH = 6

Polarogram 2 - Labile Cu, pH = 6, centrifuged 30 minutes

Polarogram 3 - pH (of 2) adjusted to 0.7

Polarogram 4 - Labile Cu, pH = 6, centrifuged 240 minutes

DPASV Polarogram Figure 7

Skead—Feb 8 - Mar 3, 1975

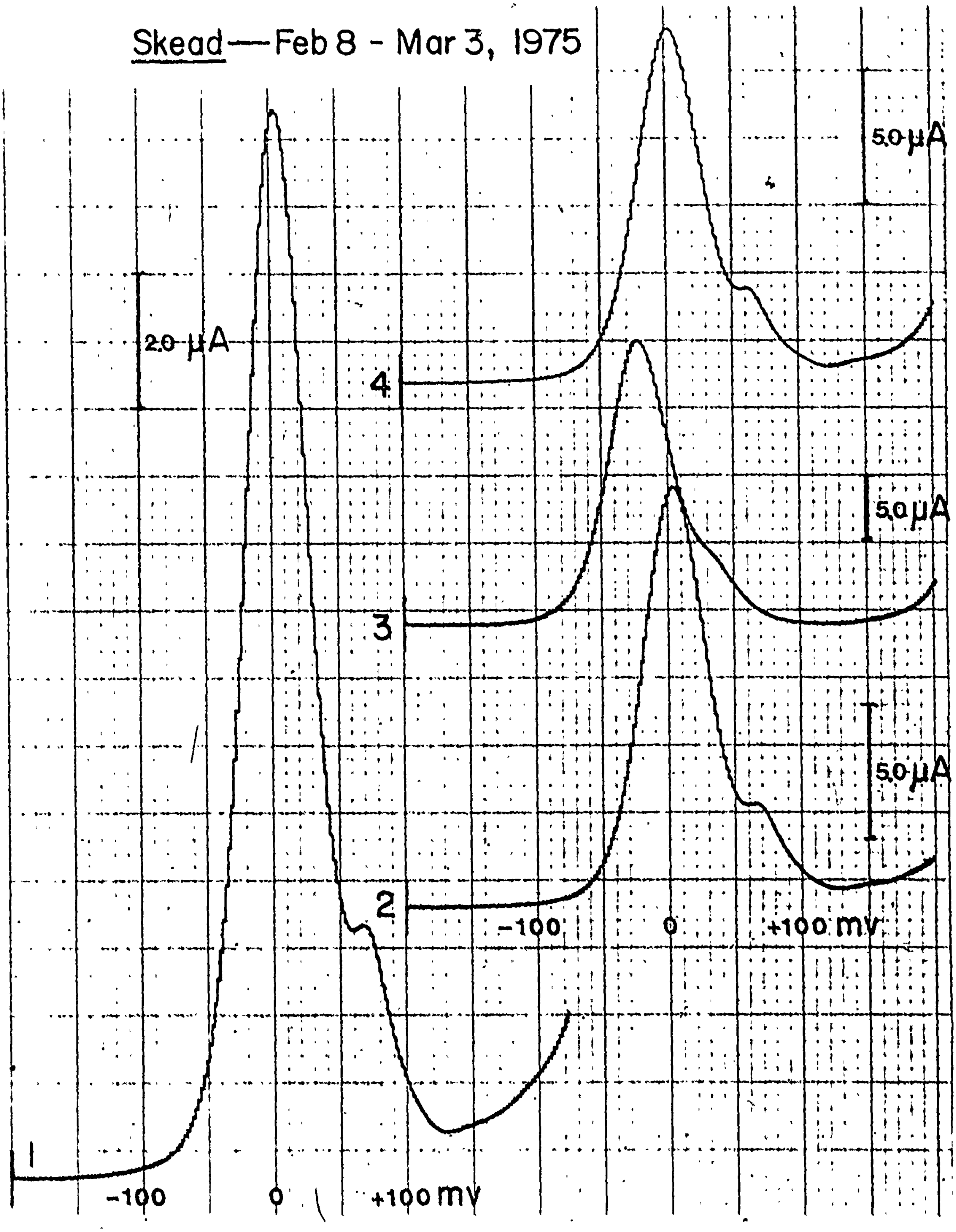


FIGURE 8 DPASV Polarogram
Duck Island, Mar. 5 - Apr. 12, 1975

Polarogram 1 - Labile Cu, pH = 6
Polarogram 2 - pH adjusted to 0.7
Polarogram 3 - Labile Cu, pH = 6,
ultracentrifuged 30 minutes
Polarogram 4 - Labile Cu, pH = 6,
ultracentrifuged 240 minutes
Polarogram 5 - pH (of 4) adjusted to 0.7

8

Duck Island — Mar 5 - Apr 12, 1975

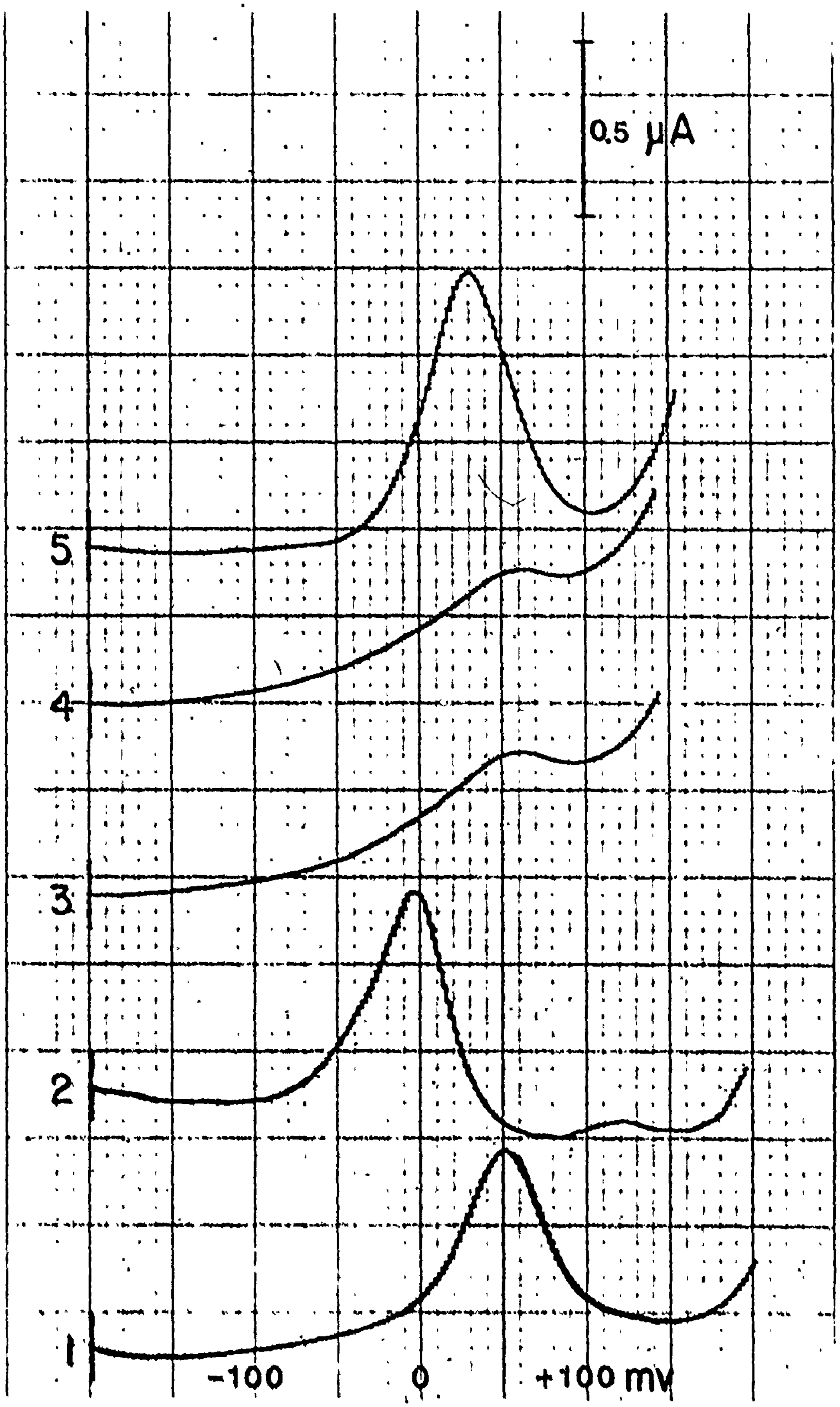


FIGURE 9 DPASV Polarogram

Verner - Feb. 8 - Mar. 7, 1975(a)

Polarogram 1 - "Labile" Cu, pH = 6

Polarogram 2 - pH adjusted to 1.7

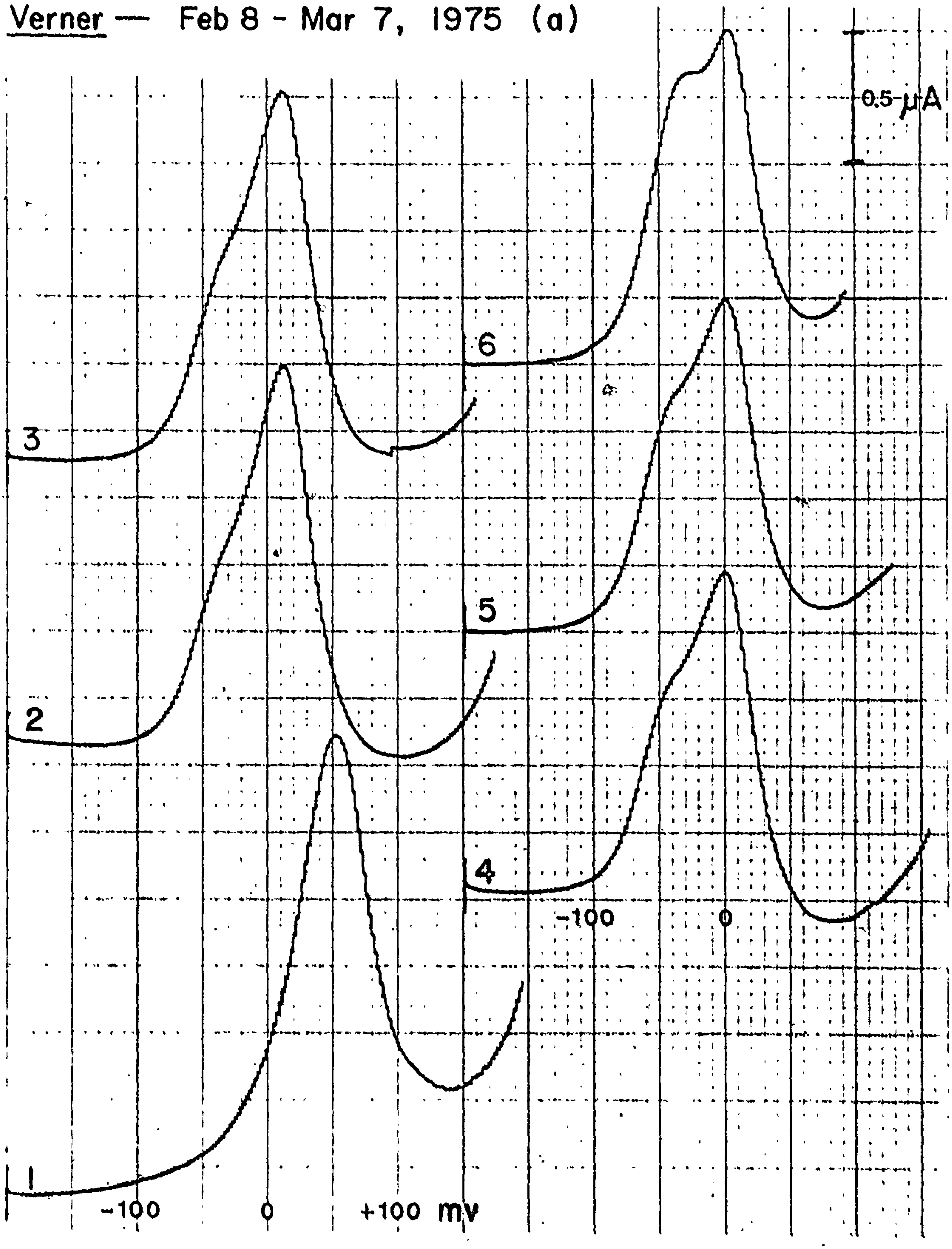
Polarogram 3 - Equilibrated an additional
20 minutes at pH = 1.7

Polarogram 4 - HNO_3 added to obtain pH = 0.7

Polarogram 5 - Equilibrated an additional
30 minutes at pH = 0.7

Polarogram 6 - 400 μM hydroxylamine hydrochloride added

Figure 9



deposition, distribution pattern of industrial emanations originating at Sudbury (Kramer, 1973; Kramer, 1975). Stations located in the outer region are affected by order-of-magnitude lower levels than those in the inner region. This is not to say that for some parameters, the levels measured are still not significantly higher than "background".

For example, the overall northern Ontario ambient atmospheric nickel level (22μg/l) is twenty-five times that of the U.S.A. Mean (Kramer, 1973)! Obviously, the nickel source (Sudbury) is playing a major role over a tremendous area.

The three sets of polarograms (Figures 7 - 9; Skead, Duck Island and Verner) give examples of results normally observed in each of the above regions. Skead, located just south of Lake Wanapitae, is within the region of major industrial influence and exhibits a large Cu peak precisely at the calibration E_p, that is, most of the filterable copper in this sample is present in the labile form, presumably as the Cu-aquo complex. The peak height when compared to calibration plots corresponds to filtered Cu analysis performed by atomic absorption within the possible errors involved (±10%). Given the low pH and high Cu normally present in these samples, this result is as expected. Allen (1974) found that a Cu-carbonato complex predominated in most natural waters, i.e., lake and ocean waters in the pH range 6 - 9. This possibility is less likely in precipitation samples where average pH values are only somewhat greater than four and alkalinity is at a low, although usually measurable value. The possible consequence of being able to determine alkalinity even at low pH will be discussed later.

Of added interest in the Skead polarograms is the small shoulder present on the anodic side of the principal Cu peak. Its existence is attributed to the presence of Cu associated with highly dispersed colloidal material for the same reasons as outlined later. The effect of ultracentrifugation for 240 minutes may be seen in polarograms 2, 3, and 4 of Figure 7 respectively, and is discussed later.

Polarograms for Duck Island and Verner samples are given in Figures 8 and 9. These stations constitute examples of precipitation collected outside the controlling influence of the Sudbury industrial region. The predominating feature of these polarograms is the presence of a measurable peak with E_p anodically shifted with respect to the E_p of the aquo-Cu species. The peak current has been found to compare well with copper concentrations measured by atomic absorption in many cases, although a significant incidence of i_p's corresponding to substantially larger and smaller comparative concentrations has also been noted. Reasons for this behaviour were investigated at length.

The possibility of NH_3 stabilization of Cu^+ has been suggested previously. Indeed, NH_3 concentrations in precipitation in the range 0.5 to 1.0 mg/l are commonly observed; however, all attempts to produce this effect using laboratory prepared copper and NH_3 solutions failed. It is evidently impossible to stabilize Cu^+ in the aqueous-acetate buffered polarographic solution. The relative stabilities of Cu^+ and Cu^{++} depend very strongly on the dielectric constant of the solution Cu^{++} being favoured in aqueous solutions due to its much higher solvation energy (Cotton and Wilkinson, 1966).

III.6.b Colloidal Association

Since Cu is not stabilized by a "normal" complex species (i.e., E_p shifted in the wrong direction) and does not occur as the aquo-Cu^{++} species, the question arises as to what other types of chemical associations may exist. Cu may be associated with highly dispersed natural colloidal material and experiments were designed to prove or disprove this theory. The occurrence of such colloids could account for the observed polarograms not only from the standpoint of electrode reaction inhibition by the surface active species, but also from kinetic reaction control and inter-metallic compound formation. The surface adsorption relationship existing between copper and colloidal material is manifested by a reaction rate which is kinetically slow relative to the polarographic reaction rate; also the diffusion of colloidal material to the HMDE during the plating step might result in incorporation of this material and hence formation of appropriate intermetallic compounds. Separation and determination of which particular factor is the ultimate cause is impossible at present, and it is probable that a complex combination of all three is in operation. Anodically shifted E_p's are consistently observed over a 100 mV range. The lack of a small shifted peak potential range is evidence for the operation of a highly variable set of conditions as might occur under various combinations of the above factors.

Some insights into the nature of the hypothesized colloids may be drawn from gross precipitation chemistry, and other observed behaviour. As with most chemical surveys, "solubility" has been operationally defined by filtration through 0.45μ membrane. As noted by Stumm and Bilinski (1973) and Stumm and Brauner (1973), this definition proves to be inadequate when considering the solubility of iron and manganese in the natural environment. On the basis of solubility product calculations, Fe^{+++} concentrations must fall in the range 0.1 to 24 μg/l (pH = 8 - 4). The fact that values in excess of this are continually measured suggests substantial supersaturation, with formation of soluble organic complexes commonly postulated as the cause.

Stumm and Bilinski (1973) have noted that in most natural surface waters, dissolved organic carbon concentration usually falls in the range 0.2 - 5 mg C per litre, corresponding to a total sum of 10^{-5} - $10^{-7.5}$ moles per litre of organic ligands. (Soluble organic carbon analysis in Ontario precipitation samples fell in the range 2.5 - 4.5 mg C/l.) They suggest that the probable high diversity of organic species means that potential complex formers will be at concentrations of 10^{-6}M or less. Since the functional groups expected to participate in complex formation and usually found in dissolved organic substances (-COOH, $-NH_2$, -OH, -SH) show little metal specificity, the coordination tendency of most ligands may be satisfied by the major divalent cations present, i.e., Ca and Mg. This concept may be applied to precipitation samples, although Ca, Mg concentrations are 1 - 3 orders of magnitude lower than in surface waters. Direct correlation between dissolved carbon analysis and ligand concentration neglects the possible presence of strong, low molecular weight ligands, which may be used to account for lake water complexing capacities as discussed later.

Just how small may the colloidal particles be? Stumm and Bilinski (1973) and Stumm and Brauner (1973) suggest that particle sizes of 100 Å or less are possible. Membrane filtration is incapable of separating such a finely dispersed phase, and it is consequently operationally very difficult to distinguish between soluble and colloidally dispersed species. Filtration experiments of high filtered iron precipitation samples (typically > 200 μg/l) using 0.1 and 0.01 μ Millipore membrane did show some loss (i.e., mass loss) of filtered Fe (10 - 20%) with each succeeding smaller pore size; however, substantial quantities still remained after the 0.01 μ (100 Å) filtration.

Colloids of this particle size will exhibit a tremendous surface area for heavy metal adsorption, either as the aquo-metal species or, quite possibly, as metal organic or metal-inorganic species. The adsorbability of trace metals is dependent on speciation; the substitution of a ligand for an aquo group will render the metal more hydrophobic and more surface seeking by reducing the interaction between the central metal ion and the remaining aquo groups. Also, hydrogen bonds may readily form at the colloid-ligand interface (Stumm and O'Melia, 1968).

III.6.c Ultracentrifugation Study

The question of just what mechanism may be used to separate such finely dispersed phases now arises. Lengweiler *et al* (1961), while conducting Fe solubility studies, reported that almost all synthetically prepared colloidal Fe could be sedimented by ultracentrifugation (93,000 g for 180 minutes). This method was considered suitable for application to precipitation samples.

Ultracentrifuging of samples at 49,000 rpm (100,000 - 200,000 g) caused various changes in observed polarographic response. In most cases, a decrease in peak height was also observed as would be expected if partial colloid sedimentation was achieved. Also, small peak potential shifts ($\sim$10 mV) towards the labile calibration potential were common, although in a significant number of cases, a shift in the opposite direction was observed (for example, Figure 8). Clearly, peak potential is strongly dependent on degree of dispersion and consequent probable degree of electrode reaction inhibition. Gross chemical composition of colloid particles may also play a role.

Curves 3 and 4 of Figure 8 illustrate the major decrease in i_p obtained after ultracentrifugation. Curves 1 and 2 (Figure 10) are polarograms of the corresponding Verner sample (Figure 9, #1) after ultracentrifuging for 30 and 240 minutes, respectively. Although not nearly so drastic reductions in i_p are observed (25% for 240 min.), the trend is in the expected direction.

III.6.d Sample Acidification

The acidification of samples to low pH may be expected to cause dissolution of reasonably soluble colloids (Fe and Mn oxides) and desorption of heavy metals. If both processes go to completion, then polarographic response similar to the acidified calibration curve (Figure 6, #4) will be obtained. In Figures 8 - 11, polarograms of acidified samples previously run at pH = 6 are displayed (see description of each figure). These polarograms also have anodically shifted peaks relative to the acidified calibration polarogram. Samples at pH = 6 exhibiting large anodic potential shifts relative to the pH = 6 calibration, similarly show the largest anodic shifts at pH = 0.7. This behaviour is found in almost all samples except those containing labile "aquo-Cu^{++}", i.e. near Sudbury samples. The Skead sample, Figure 7, contains mostly labile "aquo-Cu^{++}", which behaves "correctly" on acidification. As mentioned previously, there is a small although distinct second component present, however, yielding a shoulder on the anodic side of the main Cu peak. After acidification, this shoulder, although diminished in size, is still clearly present.

Similarly, the Duck Island and Verner samples (Figures 8 - 11), which do not contain the aquo-Cu^{++} fraction yield anodically shifted

FIGURE 10 DPASV Polarogram

Verner - Feb. 8 - Mar. 7, 1975(b)

Polarogram 1 - Labile Cu, pH = 6,
ultracentrifuged 30 minutes

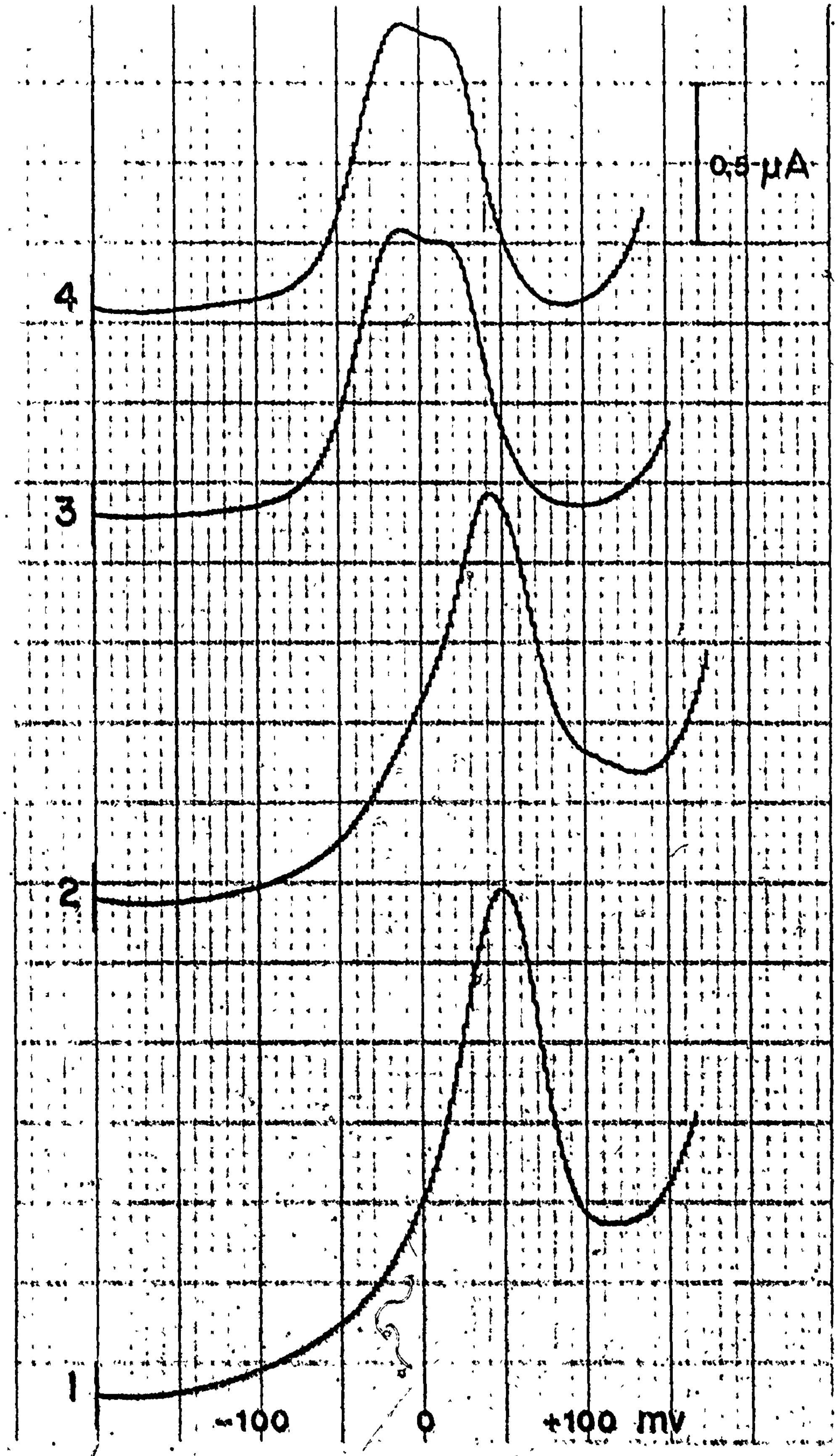
Polarogram 2 - Labile Cu, pH = 6,
ultracentrifuged 240 minutes

Polarogram 3 - pH = 0.7 (0.6 ml HNO_3 added to 3)

Polarogram 4 - 400 μm hydroxylamine hydrochlorided added

DPASV Polarogram Figure 10

Verner — Feb 8 - Mar 7, 1975 (b)



peaks. Figure 9 gives the results of a study showing the effects of the degree of acidification, and time of sample equilibration at that pH. Curve 1 is the "normal" labile Cu polarogram, while Curves 2 and 3 are for the same sample after acidification to pH = 1.7 and increasing equilibration times (2 = 10 minutes total, 3 = 30 minutes). The E_p for these peaks is shifted as mentioned above and a small shoulder on the cathodic side is evident. Curves 4 and 5 give the results after further acidification to pH = 0.7. The cathodic shoulder is now much more prominent and, most significantly, inflects at the E_p of the acidified Cu^{++} calibration polarogram. Peak height is also decreased as expected with the continued emergence of the cathodic Cu^{++} shoulder. Equilibration time plays an apparently minor role.

The colloidal material causing this polarographic behaviour is obviously affected only very slowly by highly acidic conditions. Fe colloids would be expected to dissolve almost immediately, and although Mn-oxides are more stable at low pH (Jeffries, 1974), their eventual dissolution would also be expected. The increasing cathodic shoulder size with decreasing pH would be a manifestation of this phenomenon. Addition of a reducing agent would be expected to speed such a process and Curve 6 gives the result after addition of 400 μM hydroxylamine hydrochloride and equilibration for 10 minutes. A substantial increase in the size of the cathodic Cu^{++} shoulder lends verification to this theory. Nevertheless, the anodic peak, although diminished in height, still remains. The colloid in the Verner sample is obviously at least a two-component system, one of which is extremely resistant to low pH and reducing conditions, and is still sufficiently surface active to inhibit electrode reaction. An alumino-silicate analogous to clays might fit this description, although with the extremely small quantities of mass involved, verification by conventional means (i.e., X-ray identification) would be impossible. With an average particle size less than 0.01 μ, even electron microscopic techniques are inadequate.

Ultracentrifuging of the Verner sample shows that the acid soluble (reducible) component is less affected, since on acidification, the cathodic Cu^{++} portion of the stripping peak becomes dominant. Alteration of the adsorption character due to centrifuging would be the only other possible (although improbable) explanation.

III.6.e Sample Storage

Figure 11 gives an example of a phenomenon which has been common to almost all samples tested. The sample preparation procedure calls for 0.45 μ filtration into a Pyrex storage vessel, normally a 500 ml Erlenmeyer flask. It has been found that on aging in these flasks, the peak height of subsamples gradually decreases with time. Similarly, E_p shifts with time. Storage of the Verner sample for 2 days gave a polarogram almost exactly equivalent to that obtained for ultracentrifuging (240 minutes), both for the pH = 6 and 0.7 situations. Adsorption of colloidal

FIGURE 11 DPASV Polarogram

Verner - Feb. 8 - Mar. 7, 1975(c)

Polarogram 1 - Labile Cu, pH = 6, sample stored 2 days in glass flask prior to analysis

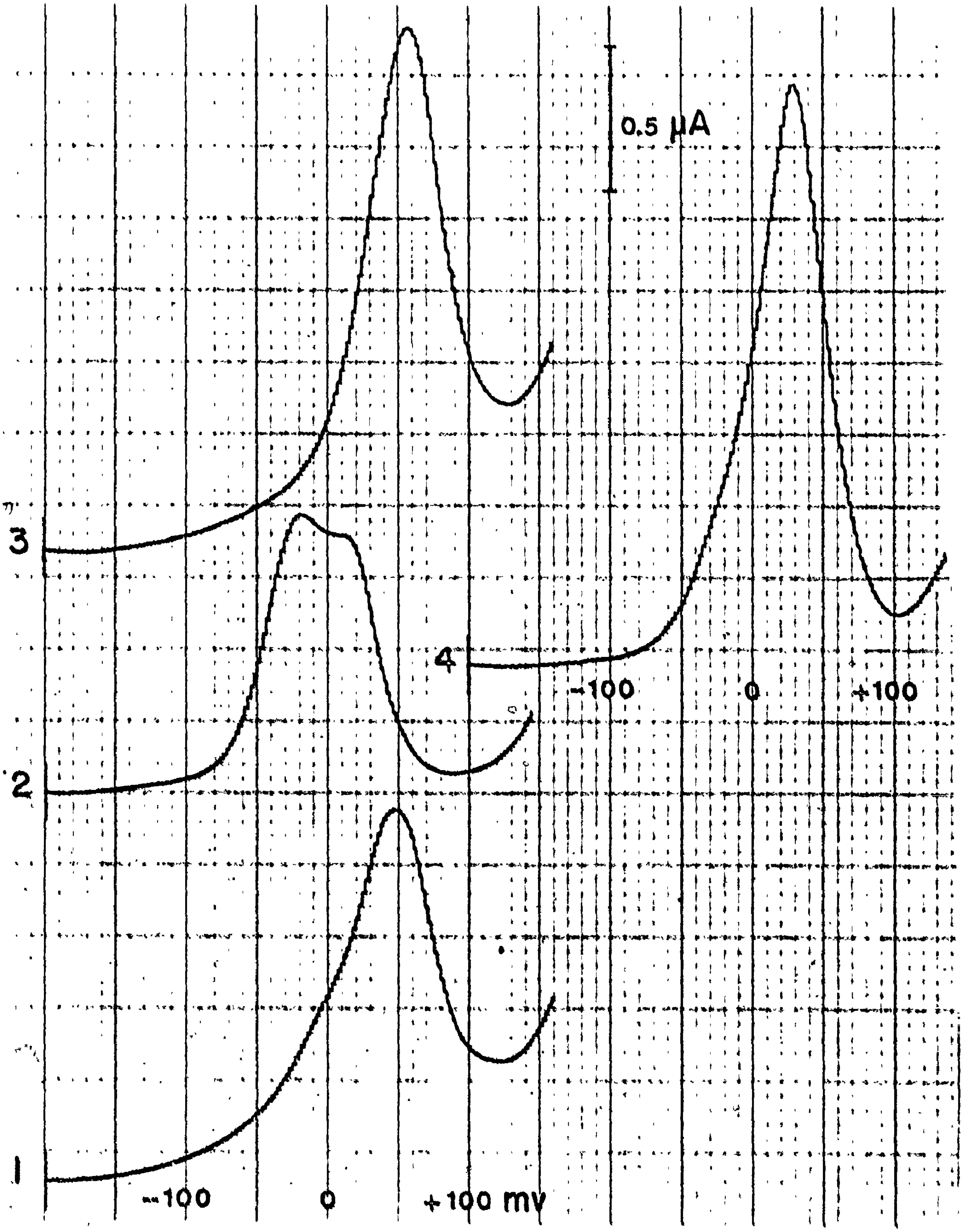
Polarogram 2 - pH adjusted to 0.7

Polarogram 3 - Labile Cu, pH = 6, same as 1 except storage container surface disturbed with a teflon spatula

Polarogram 4 - pH adjusted to 0.7

DPASV Polarogram Figure II

Verner — Feb 8 - Mar 7, 1975 (c)



material onto the flask surface was hypothesized as the cause, and disturbing of the surface with a Teflon spatula suggested as the obvious test. After scraping of the inner flask surfaces and agitation of the sample to assure homogeneity, a polarogram almost exactly equivalent to that of the newly filtered sample was obtained (Curves 3 and 4, Figure 11). This extremely simple experiment of an almost universally observed phenomenon (with respect to precipitation samples) lends strong support to the hypothesis of the colloidal association of heavy metals in precipitation. Needless to say, there are further implications with regard to the handling of such samples for any type of analysis if accurate results are desired.

III.6.f Synthetic Colloid States

Having obtained evidence for the existence of colloidal association, experiments were initiated in an attempt to simulate nature; that is, produce the same effects noted previously with synthetic samples. In the pH range of most precipitation (4 - 6.5) two common colloidal systems will exhibit surface charges which allow the adsorption of cations. Fe oxides generally have an isoelectric point in the pH range 6 - 7, although some specific adsorption of ions below this pH has been reported. Mn-oxides have a much lower isoelectric pH and consequently adsorb cations more strongly. Other systems which may play a role are SiO_2 with a pH (ZPC) = 2.0 and highly dispersed clays (pH(ZPC) = 2 - 4.5). As mentioned previously, the first two of these (Stumm and Morgan, 1970) should be acid soluble while the last two may be more resistant. The effect played on any of these highly dispersed systems on ASV response has not been documented. It has been noted that precipitation is commonly "supersaturated" with "soluble" iron as calculated from iron hydroxide solubility when such solubility is defined by 0.45 μ membrane filtration. Values of filtered Fe greater than 100 μg/l are common. Routine determination of Mn, unfortunately, has not been carried out. A few samples have been analyzed and the results are presented in Table XI. Lazrus *et al* (1970) reported a mean filtered Mn concentration of 12 μg/l for U.S. precipitation. Considerable data are available for atmospheric concentrations of Mn and Fe obtained through the high volume filter sampling and analysis (Harrison *et al*, 1971 b; Miller *et al*, 1972; Winchester and Nifong, 1971). Manganese precipitation concentrations show considerable variability as is commonly observed for other heavy metals. On the basis of this small number of samples there is no obvious relationship between concentration and proximity to Sudbury, as has been shown for Fe, Cu and Ni. Quantities of Mn and Fe emitted by the International Nickel Company's 1200 ft. stack are also given in Table XI. The Fe:Mn ratio is three to eight times greater than that calculated for average crustal abundances, while determination of the same quotient for high volume filters collected in a variety of industrial areas yields values that are two to three times less. This may only occur if there is a rapid differential dry fall-out of Fe with respect to Mn near the source, and it must also follow that Mn is associated with the much finer aerosol fraction.

TABLE XI

MANGANESE IN THE ATMOSPHERE

Sample	Precipitation Concentration (filtered) -- µg/l.	Source
USA Average	12	(Lazrus *et al*, 1970)
NRC	50	McMaster Analysis (May, 1975)
S. S. Marie	32	
Espanola	48	
River Valley	27	
Sudbury South	< 5	
Skead	33	
Verner	39	
Gore Bay	10	
South Baymouth	18	
Skead	< 5	McMaster Analysis (Feb., 1975)
Verner	10	
Duck Is. (Total)	12	
Duck Is. (Tower)	37	

Average Crustal Abundances for Fe and Mn: (Handbook of Chemistry and Physics)

Fe = 50,000 mg/kg

Mn = 1,000 mg/kg

Fe : Mn = 50

TABLE XI (cont'd)

Sample	Atmospheric Particulate Concentration			Source
	Mn ($\mu g/m^3$)	Fe ($\mu g/m^3$)	Fe : Mn	
NW. Indiana	0.15	4.77	32	Harrison et al, (1971b)
Chicago	0.07	1.6	23	Winchester and Nifong (1971)
East Chicago	0.28	5.5	20	
Milwaukee	0.12	1.9	16	
Tawas Pt. (Michigan)	0.006	0.13	22	McMaster Analysis
Lake Huron	0.02	0.30	15	
Hamilton North	0.32	6.5	20	Ontario Ministry of the Environment
Hamilton South	0.17	3.6	21	
Sudbury	0.02	3.7	185	
North Bay	0.02	0.7	35	
Ottawa	0.06	1.1	19	
S. S. Marie	0.04	1.6	40	

INCO Stack Emissions

Sampling Date	Mn (lb/hr)	Fe (lb/hr)	Fe : Mn	Source
June 8, 1973	4.1	678	165	Ontario Ministry of the Environment
June 21, 1973	1.5	404	269	
July 4, 1973	2.2	658	299	
July 13, 1973	1.6	660	413	

Predictably Fe:Mn values decrease with distance from Sudbury, as is shown for Sudbury, North Bay, Sault Ste. Marie and Ottawa values in Table XI.

Mn and Fe colloids are the most probable naturally occurring materials which could account for this behaviour. Average filtered Fe levels of 36 μg/l and Mn (26 μg/l, Table XI) are present. Stumm and Morgan (1970) point out that natural iron and manganese colloids (δ-MnO_2 and γ-$FeOOH$) may exhibit surface areas up to 300 m^2/g and absorb various heavy metals in the proportion 0.3 - 1.0 moles of heavy metal per mole of adsorbing species. If it is assumed that half the observed Fe and Mn is, in fact, truly soluble, there still remains approximately 4×10^{-7} M of total adsorbing material. In regions outside the immediate Sudbury area, Cu and other heavy metals generally occur in concentrations at or below this level. Hence it is then chemically possible for the colloidal association to exist.

Although little Mn data are available, it is perhaps very significant that <5 μg/l of filtered Mn were detected for the two near-Sudbury stations in Table XI. It is possible that the overwhelming Cu concentrations present in these samples resulted in Mn colloid saturation and destabilization. Coagulation of the colloid would result in its removal by filtration.

Manganese and iron colloids (individually and mixed) were prepared as described earlier. Cu addition (0.1 μM) was carried out prior to Mn and Fe oxide precipitation, and in some cases SiO_2 and Al^{+3} were added (50 μg/l). Polarograms of these synthetic colloidal systems are given in Figures 12 - 15. Figure 12, curves 1 and 2, illustrates polarographic response of 0.1 μM Cu^{++} in the absence of colloidal material. The expected i_p and E_p are obtained. Curves 3 and 4 give the response of a mixed colloid system (Mn, Fe, Al, SiO_2) in the absence of Cu. The failure to obtain any significant polarographic response is important, since it verifies that the presence of Cu is necessary to obtain polarograms of the type previously discussed; that is, observed shifted peaks are caused by colloidally associated Cu and not just by the colloid itself. The small peak obtained for the acidified, no Cu^{++} case(No. 4) is the normal blank level. Curves 5 and 6 give the composite case, i.e., mixed colloid plus Cu^{++}. The peak is somewhat "blurred" out on the anodic side although the differences between it and the 0.1 μM Cu^{++} calibration peak are very small. Succeeding experiments proved more successful and it must be assumed that the presence of Al and SiO_2 (at 50 μg/l) in this experiment prevented colloidal association of Cu with the Fe and Mn oxides, or more probably, altered the surface chemical properties of the colloid to a sufficient degree to alter reaction inhibition during the stripping step.

Figure 13 illustrates the case of Mn colloid plus Cu. After preparation, this system was aged in polyethylene for 3 weeks and then analyzed. Curve 1 represented a labile Cu determination at pH = 6. Almost no discernable peak is obtained, although some Cu is present, as verified by the

FIGURE 12 DPASV Polarogram
Mixed Colloid Experiment

Polarogram 1 - 0.1 μM Cu (cf calibration), labile Cu, pH = 6

Polarogram 2 - pH (of 1) adjusted to 0.7.

Polarogram 3 - Mixed colloid, 50 μg/l Mn-T, Fe-T, SiO_2-T, Al-T, no Cu^{++}

Polarogram 4 - pH (of 3) adjusted to 0.7

Polarogram 5 - Mixed colloid as in 3 plus 0.1 μM Cu^{++}

Polarogram 6 - pH (of 5) adjusted to 0.7

DPASV Polarogram Figure 12

Mixed Colloid Experiment

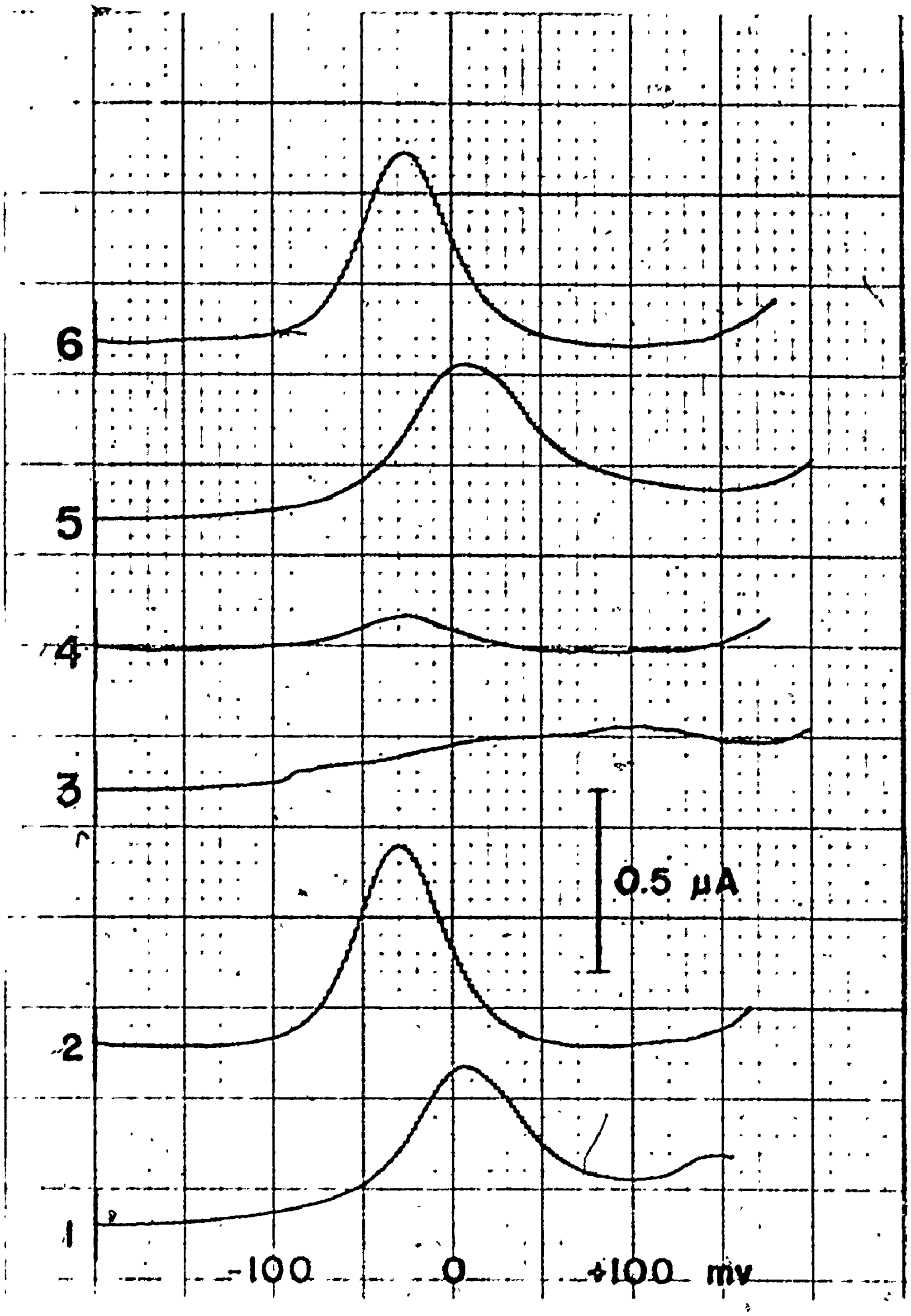


FIGURE 13. DPASV Polarogram

Mn Colloid (50 μg/l Mn-T)

Cu-T = 0.1 μM

(aged 3 weeks in polyethylene)

Polarogram 1 - Labile Cu, pH = 6

Polarogram 2 - pH (of 1) adjusted to 0.7

Polarogram 3 - Labile Cu, pH = 6, storage container surface disturbed with a teflon spatula

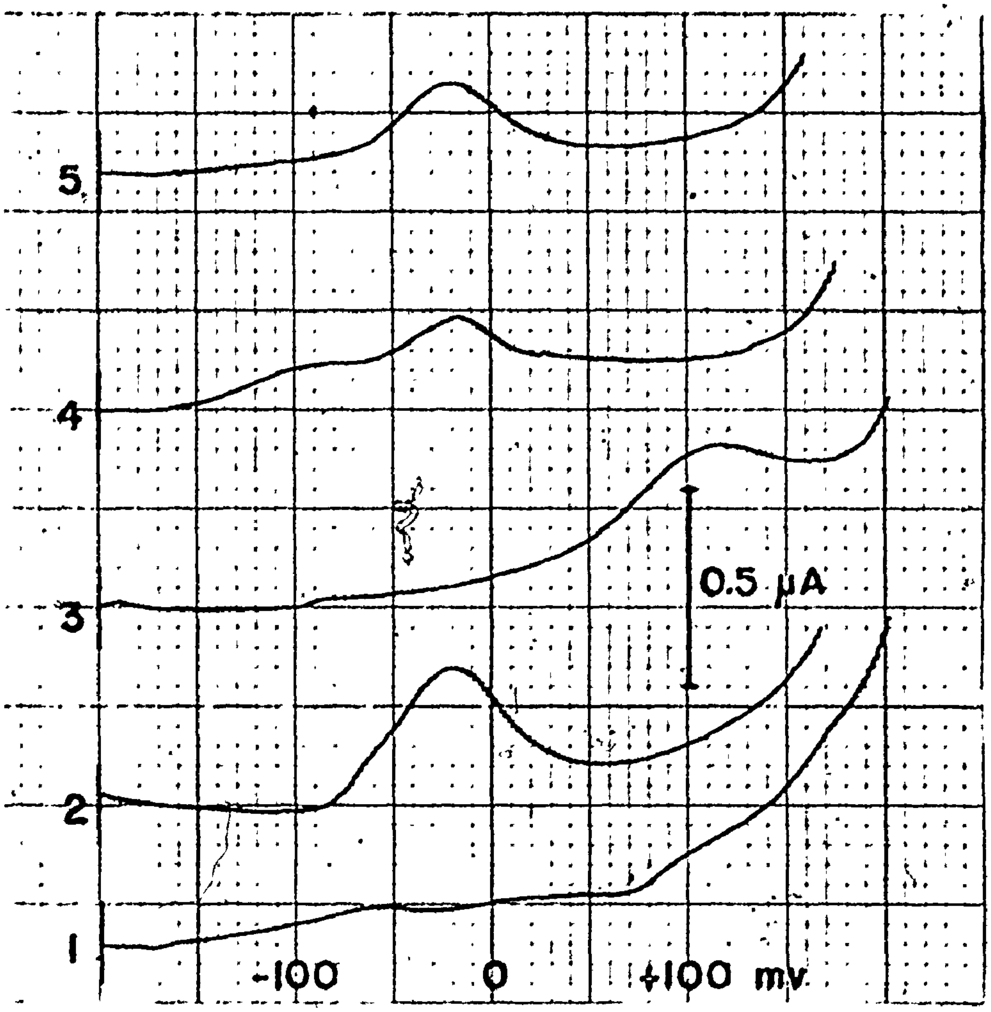
Polarogram 4 - pH (of 3) adjusted to 0.7

Polarogram 5 - 400 μM hydroxylamine hydrochloride added

DPASV Polarogram Figure 13

Mn Colloid (50 μg/l Mn-T)

Cu-T = 0.1 μM



appearance of a peak on acidification (No. 2). Scraping of the storage container walls with a Teflon spatula, followed by re-analysis gave Curve 3. A small peak with a highly anodically shifted E_p is observed. This bears considerable resemblance to natural samples. Acidification and addition of a reducing agent failed to retrieve all the Cu that should have been present; this may be attributed to a lack of sample homogenization after scraping with the spatula.

Figures 14 and 15 illustrate two separate experiments involving mixed Fe and Mn colloids with 0.1 μM Cu. Once again anodically shifted labile Cu peaks (Curve No. 1 in both cases) are observed, with storage time playing an apparently important rôle in the i_p obtained (Figure 14, storage = 3 weeks; Figure 15, storage = 2 days). Complete Cu retrieval is obtained on acidification (Curve No. 2). The Fe, Mn colloids dissolve at low pH as expected; however, the i_p obtained in the labile Cu case must then be considered a primary function of colloid particle size and dispersion. That is, the sample stored three weeks, having had much longer time for colloid flocculation and equilibration, behaves polarographically different. Storage container scraping and homogenization yield morphologically different polarograms (Curves No. 3 in each Figure), giving further evidence of the complex relationship existing between colloid particle size and dispersion (and composition?) and observed polarographic response. In particular, it is evident that the degree of anodic potential shift is a direct function of dispersion and probably surface activity, although quantification of this effect is impossible at present.

FIGURE 14 DPASV Polarogram

Mixed Fe, Mn Colloid (50 μg/l Fe-T, Mn-T)

Cu-T = 0.1 M

(aged 3 weeks in polyethylene)

Polarogram 1 - Labile Cu, pH = 6

Polarogram 2 - pH (of 1) adjusted to 0.7

Polarogram 3 - Labile Cu, pH = 6, storage container surface disturbed with a teflon spatula

Polarogram 4 - pH (of 3) adjusted to 0.7

DPASV Polarogram Figure 14

Mixed Fe, Mn Colloid (50 μg/l Fe-T, Mn-T)

Cu-T = 0.1 μM

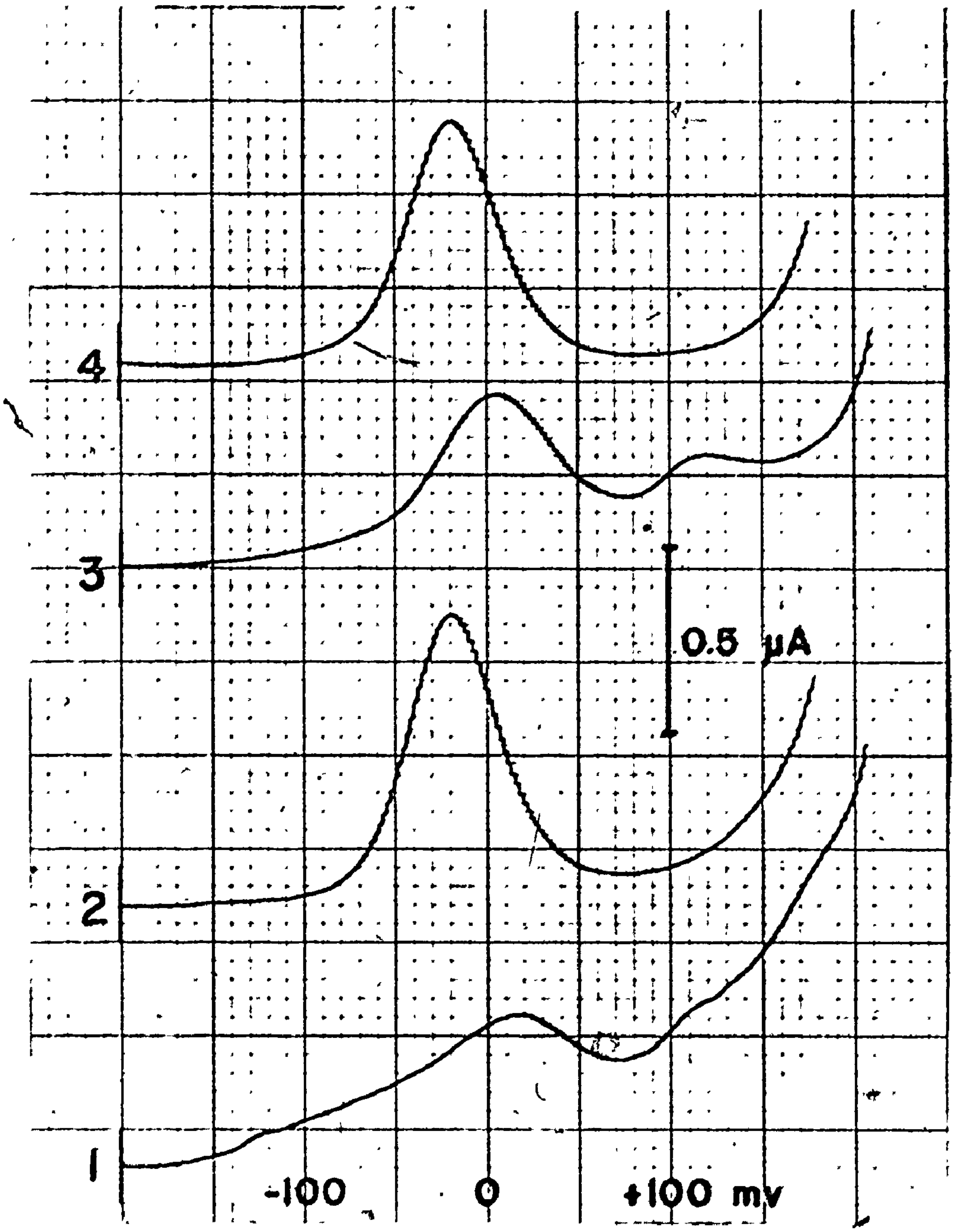
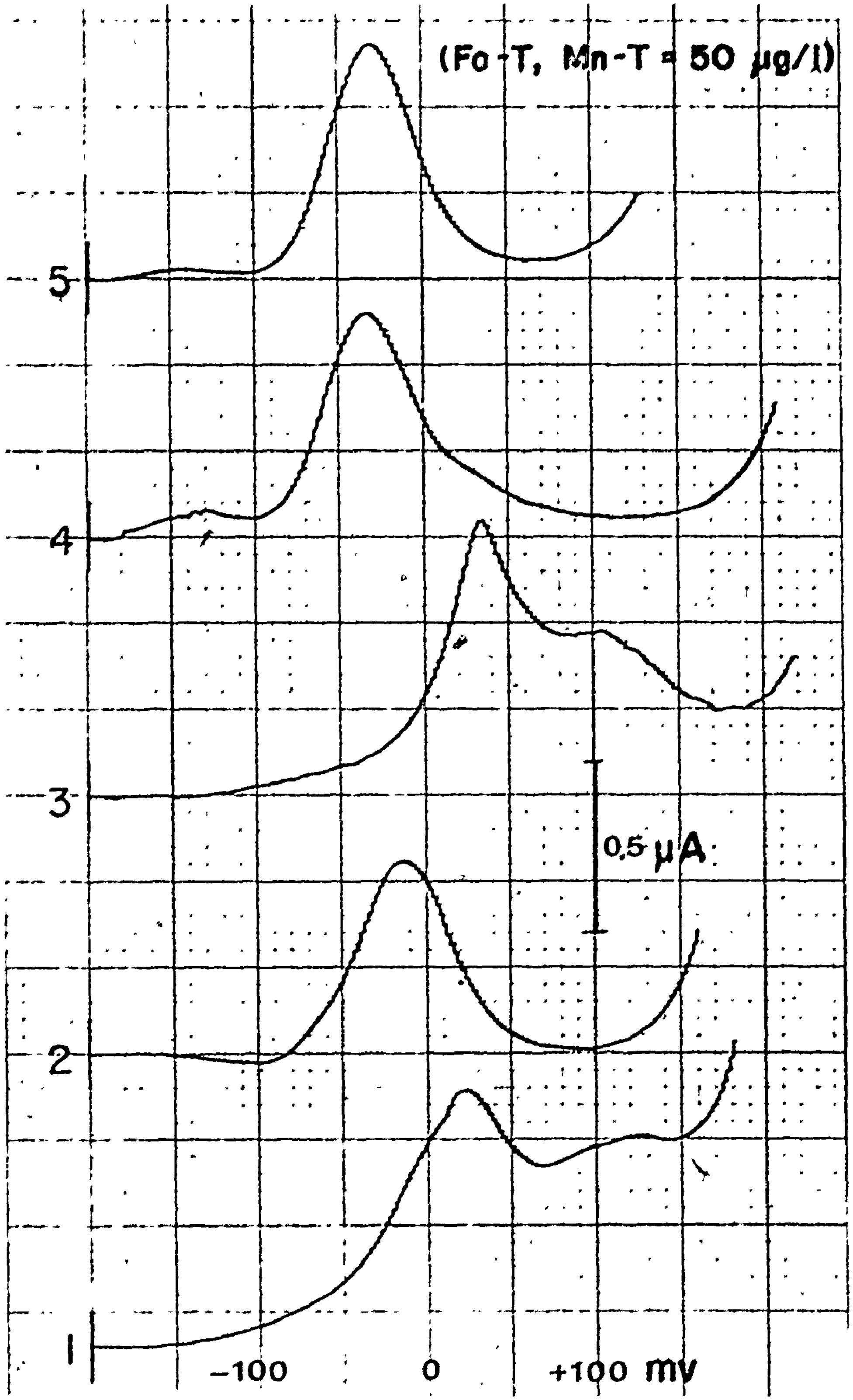


FIGURE 15 DPASV Polarogram
Fe, Mn Colloid, Cu-T = 0.1 μM
(50 μg/l Fe-T, Mn-T)

Polarogram 1 - Labile Cu, pH = 6
Polarogram 2 - pH adjusted to 0.7
Polarogram 3 - Labile Cu, pH = 6, storage container surface disturbed with a teflon spatula
Polarogram 4 - pH (of 3) adjusted to 0.7
Polarogram 5 - 400 μM hydroxylamine hydrochloride added

DPASV Polarogram Figure 15

Fe, Mn Colloid — Cu-T = 0.1 μM



Is a colloidal association of heavy metals reasonable from a chemical standpoint? The colloid particles may be considered as hydrous metal oxides, with surfaces represented by -Me-OH. Surface charge is regulated by the degree of ionization (proton transfer) within the hydration layer, which is in itself a function of the electronegativity of the metal in question. Surface charge is consequently pH-dependent with net negative values predominating at high pH and positive values at low pH. At a specific pH, the net surface charge will be zero, i.e., the pH(ZPC); above this pH, coulombic adsorption of cations will occur. As mentioned previously, iron, manganese, silica and "clay" colloids all have sufficiently low pH(ZPC) to allow coulombic adsorption of cations in the pH range of precipitation. Specific adsorption analagous to complex formation will also be important, with those species of low pH(ZPC) being most affected. Such specific adsorption involves proton transfer, which may be visualized as follows:

$$\text{-Me-OH} + Cu^{++} \longrightarrow \text{Me} - OCu^{+} + H^{+} \qquad (10)$$

The energy released by such a reaction may be large enough to permit adsorption to occur, even against electrostatic repulsion; this phenomenon is manifested in finite adsorption of certain anions and cations above and below the pH(ZPC) of the metal in question respectively, and has been previously reported (Jeffries, 1974; Murray et al, 1968). In general, adsorption of oppositely charged species leads to colloid destabilization, due to surface charge reduction; in the case of specific adsorption, surface charge reversal may occur, causing colloid restabilization.

Iron and manganese commonly occur in concentrations exceeding expected "solubility" levels, and thus their presence as colloids is reasonable. The presence of an alumino-silicate clay-like colloid is feasible though unproven. Certainly the scavenging of natural ultra-fine aerosol by precipitation serves as a ready mechanism for the development of a colloidal system. Considering the average pH of northern Ontario precipitation (4 - 5), only two of these (Mn and "clay") will have a substantial cation association. Iron oxides have pH(ZPC) (6.5 - 8.5) that are too high. Support for this hypothesis was obtained experimentally where it was found that simulation of the unusual polarograph response of natural samples could not be obtained using only Fe colloids. The presence of Mn, either alone or mixed with Fe, was necessary to produce the desired response. Testing of clay colloids was not attempted due to an inability to produce suspensions of small enough particle size and consequently great enough stability.

The association of heavy metals with Mn oxide colloids has been studied by several authors (Jeffries, 1974; Murray et al, 1968; van den Berg, 1975; Morgan and Stumm, 1964; Murray, 1973) as a function of pH. In the pH range of natural waters, specific adsorption of the first transition series of heavy metals occurs. Cobalt is most strongly adsorbed, followed by copper, nickel and zinc. Van den Berg (1975) has shown that adsorption from mixed metal solutions proceeds with the most strongly adsorbed metals affected the least, while those with smaller affinities show a marked adsorption reduction. This phenomenon, coupled with the relative amounts of metal available for adsorption, must be considered in developing an adsorption model to explain observation. Cobalt in precipitation samples normally occurs at barely detectable levels, i.e., 1 μg/l or less and thus, when in competition with other metals at 10 - 20X higher concentrations, does not influence their adsorption. Use of copper as an indicator of colloid association is thus reasonable, given its relatively strong affinity for hydrous Mn-oxides and its consistently observed concentration levels (10's of μg/l except near Sudbury), which place it at the same or higher level than most other metals. At any given pH and Mn colloid level, a maximum adsorption capacity exists, which will depend on the relative and absolute concentrations of adsorbable species. Near Sudbury, the high concentration of all "soluble" metal species suggests a saturation of this adsorption capacity, leaving an excess of metal ion as observed in the ASV polarograms. It should be noted that adsorption of Ca^{++} and Mg^{++} is very weak, and alkali metal association occurs by coulombic attraction alone. Their interference in heavy metal association will be minimal, which is in direct contrast to that expected for naturally occurring, non-specific, complexing agents.

III.6.g ASV of Lake Water - Complexing Capacity Determination

It is instructive to compare the polarographic behaviour of lake water samples to that of precipitation. The basic differences in gross chemistry between the two should be recalled; that is, lake waters are normally higher in pH, alkalinity, and conductivity, while lower in heavy metals. Beyond this is the ubiquitous presence of biological material, including not only that associated with primary and secondary production (phytoplankton, zooplankton and associated by-products) but also decay products (humic, fulvic acids, etc.). In the overall chemical spectrum, a "hard-water" highly productive lake may be considered at one end with precipitation occurring at the other. Lakes which fall in the middle category have relatively weaker chemical and pH buffering capacities than the "hard-water" end member, and for those with very small capacities, an approach to the composition of precipitation is possible.

This is, in fact, what has happened to several Shield lakes near Sudbury. As mentioned previously, proximity to Sudbury (controlling degree of contaminant input) coupled with small buffering capacities has resulted in primary production reduction to insignificant levels. Studies of this situation (Conroy, 1971; Conroy et al, 1974; Semkin, 1975) have pointed out the interesting fact that two lakes in very close proximity are often affected in very different ways. It must be presumed that the less affected lake has a much higher buffering capacity, resulting perhaps from the presence of a calcareous glacial till or some other mediating factor.

Labile copper polarograms of productive lakes are almost invariably flat, that is, no labile copper is detected. Analysis of corresponding digested samples show that low level Cu is indeed present, so that in order to obtain the flat labile metal polarogram, strong, probably organic, complexing of the copper must be assumed. The presence of Cu in association with colloids or as a carbonate, or hydroxy complex (Allen, 1974) would yield an appropriate polarographic peak. The organic complexing of copper has lead to the development of the concept of complexing capacity which may be considered analagous to buffering capacity. A lake with a high complexing capacity should be able to withstand the input of toxic metals to a much greater degree than one with a low or zero capacity.

The complexing capacity of several lakes in the region northeast of Sudbury was measured (Table XII). Lake pH, alkalinity, sulphate and chlorophyll a concentrations and Secchi disc depth are also included. An extended discussion of the limnogeochemistry of these lakes is provided by Semkin (1975). Similar determinations have been made by Chau (1973) and Chau et al (1974) and are included for comparison. Clearly, hard-water lakes, i.e., those with substantial alkalinity including Chau's Great Lakes samples, have consistently higher complexing capacities. Chlorophyll a and Secchi disc transparency values are qualitatively indicative of primary productivity levels. Large chlorophyll a concentrations and small Secchi disc values usually correspond to high algae levels. Data in Table XII show that, on average, lakes with very low chlorophyll values and large Secchi measurements (i.e., low productivity situations) have low complexing capacities. Lake Maskinonge has a substantial chlorophyll a concentration (0.59 mg/m^3) since it is one link in a "flow-through" series of lakes, with upstream members having a much higher productivity. Low chlorophyll a values for Lady Evelyn and Emerald Lakes may be attributed to productivity control by nutrient limitation; these lakes are distant from Sudbury and so atmospheric input of nutrients is minimal. Considering the error present in the complexing capacity determination (~15%), any lake with a value of less than 0.1 μmole Cu/litre may be considered "environmentally sensitive". Continued loading of acid precipitation and heavy metals will cause a further decline in productivity and water quality. Donald, George and Johnny Lakes have a "zero" complexing capacity. Labile copper was detected in each of these lakes under the imposed experimental conditions. Interestingly, the labile Cu

TABLE XII

THE COMPLEXING CAPACITY OF LAKE WATER

Lake	Alkalinity (meq/l)	pH	Surface SO_4 (mg/l)	Chlorophyll *a* (mg/m^3)	Secchi (ft)	Complexing Capacity (μmole Cu/l
Donald	0.013	4.55	18.7	0.07	48	0.02
Maskinonge	0.185	5.50	9.7 - 15.8	0.59	27	0.07
Chiniguchi	0.117	4.72	20.5	0.00	29	0.09
Capreol	0.030	5.90	13.0	1.47	20	0.15
Laundrie	0.137	4.70	10.9	1.61	12	0.18
Ashigami	0.147	6.25	14.3 - 17.7	2.42	14	0.18
Fraleck	0.157	5.24	10.0	0.95	15	0.31
Murray	0.159	5.81	10.5 - 14.9	0.95	21	0.37
Wanapitei	0.348	6.84	12.8	0.95	15	0.37
Temagami	0.152	6.20	7.7	-	33	0.40
Red Cedar	0.304	6.70	8.5	1.32	18	0.43
Lady Evelyn	0.160	6.40	12.3	0.37	23	0.44
Diamond	0.207	6.40	2.5	-	23	0.46
Emerald	0.103	6.50	19.6 - 20.7	0.15	38	0.48
Rabbit	0.312	7.40	13.9	1.39	20	0.70

Lake	Complexing Capacity (μmole Cu/l)	Source
Vermillion	0.43	(Chau *et al*, 1974)
Johnny	0	
Robinson	0.14	
Windy	0.45	
Whitefish	0.63	
Penage	0.47	
Fairbanks	0.09	
George	0	
Hamilton Harbour	0.70 - 1.00	
Hamilton Sewage Effluent	1.80 - 2.50	
Niagara River	0.44 - 0.58	
Lake Ontario	0.45	
Lake Erie	0.15 - 0.73	

polarogram for Donald Lake had an obvious anodic shoulder, as did low level copper-spiked (0.2 μM) aliquots of Maskinonge, Chiniguchi and Capreol. It is apparent that these lakes with zero or extremely small Cu complexing capability are approaching precipitation in their polarographic behaviour.

III.6.h Precipitation - Surface Water Interaction

The interaction between lake and precipitation water may be summarized as follows: Precipitation falling directly into surface water systems containing both particulate and "soluble" Cu^{++} (either "free" or in colloidal association) will supply this material to their internal geochemical cycles. In the case of most natural, uncontaminated waters, the particulate material may be expected to settle to the bottom and sediment; partial dissolution of particulates might occur in extremely acidic situations, although cases in which surface waters have a lower pH than precipitation will be very rare. The "soluble" copper, on the other hand, will be available for complexing with any available ligands and/or as a toxic agent for biological activity. This applies to both "free" and colloidally associated copper. The displacement of copper from colloids by sufficient concentrations of weak ligands, and by even very low levels of strong complexing agents, has been accomplished in the laboratory. The colloidal material may be expected to eventually flocculate under the influence of higher ionic strength and biological activity, although since a measureable alkalinity still exists even at low pH, the presence of a highly dispersed phase acting as a H^+ sink must still exist.

III.6.i Determination of Zn, Cd, Pb, Cu

Cu is more strongly adsorbed by Mn oxides than Zn or Cd, though perhaps not quite as strongly as Pb. Thus it is a good assumption that these other metals in precipitation will behave in much the same fashion in the overall biogeochemical cycle. By changing the plating potential in the polarographic analysis to -1.200 V (Vs SCE), all four of these metals may be simultaneously deposited and a subsequent stripping scan produces a separate peak for each metal in turn (E_p : Zn (-1000 mV), Cd (-586 mV), Pb (-408 mV), Cu (+4 mV)). Analysis of this type was carried out on a variety of precipitation samples and illustration of the results obtained given in Figures 16 and 17. Several aspects of these polarograms should be noted. First, Number 3 of Figure 16 is a typical polarogram and illustrates normal polarographic response under ideal "clean" conditions. In all other polarograms, labile Zn is measured with minor variation in E_p (±4 mV). This is in accord with observations by Chau and Lum-Shue-Chan (1974), who even found labile Zn in highly contaminated Hamilton Harbour waters. E_p's for Cd and Pb fall at the same value as that of the calibration, with the exception of Gore Bay (Figure 17, No. 2). It is then probable that these metals are present almost exclusively as the aquo-metal species. Two irregularities are evident. First, the Gore Bay sample behaves in the manner expected when an excess of complexing agent is present. Both Cd and Pb have cathodically shifted E_p's, while there is almost no peak for Cu at all. The results may be explained if sample contamination by some organic material is assumed. The Gore Bay sampler is located at the Gore Bay airport and contamination resulting from air traffic or grounds upkeep (fertilizers, pesticides, etc.) is possible.

FIGURE 16 DPASV Polarogram
4 Metal Analysis

Polarogram 1 - Skead, May, 1975
Labile Metals, pH = 6

Polarogram 2 - Espanola, May 1975
Labile Metals, pH = 6

Polarogram 3 - Calibration
Labile Metals, pH = 6

Zn = 40 μg/l
Cd = 4 μg/l
Pb = 12 μg/l
Cu = 40 μg/l

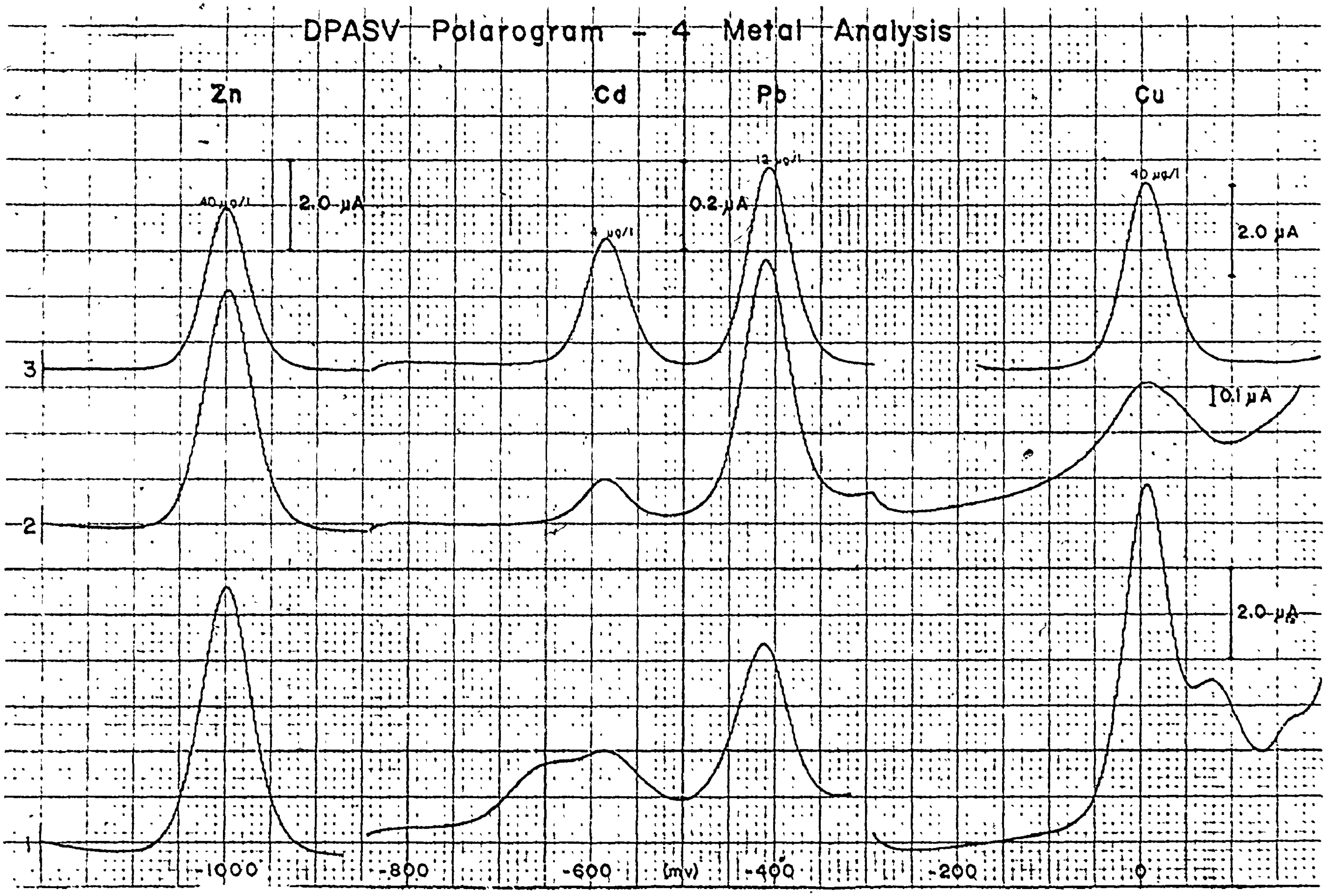

DPASV Polarogram - 4 Metal Analysis
Zn
Cd
Pb
Cu
40 µg/l
2.0 µA
4 µg/l
0.2 µA
12 µg/l
40 µg/l
2.0 µA
0.1 µA
2.0 µA
3
2
1
-1000
-800
-600
(mv)
-400
-200
0

FIGURE 16

FIGURE 17 DPASV Polarogram

4 Metal Analysis

Polarogram 1 - Verner, May 1975

Labile metals, pH = 6

Polarogram 2 - Gore Bay, May 1975

Labile metals, pH = 6

Polarogram 3 - NRC, Traverse Lake, May, 1975

Labile metals, pH = 6

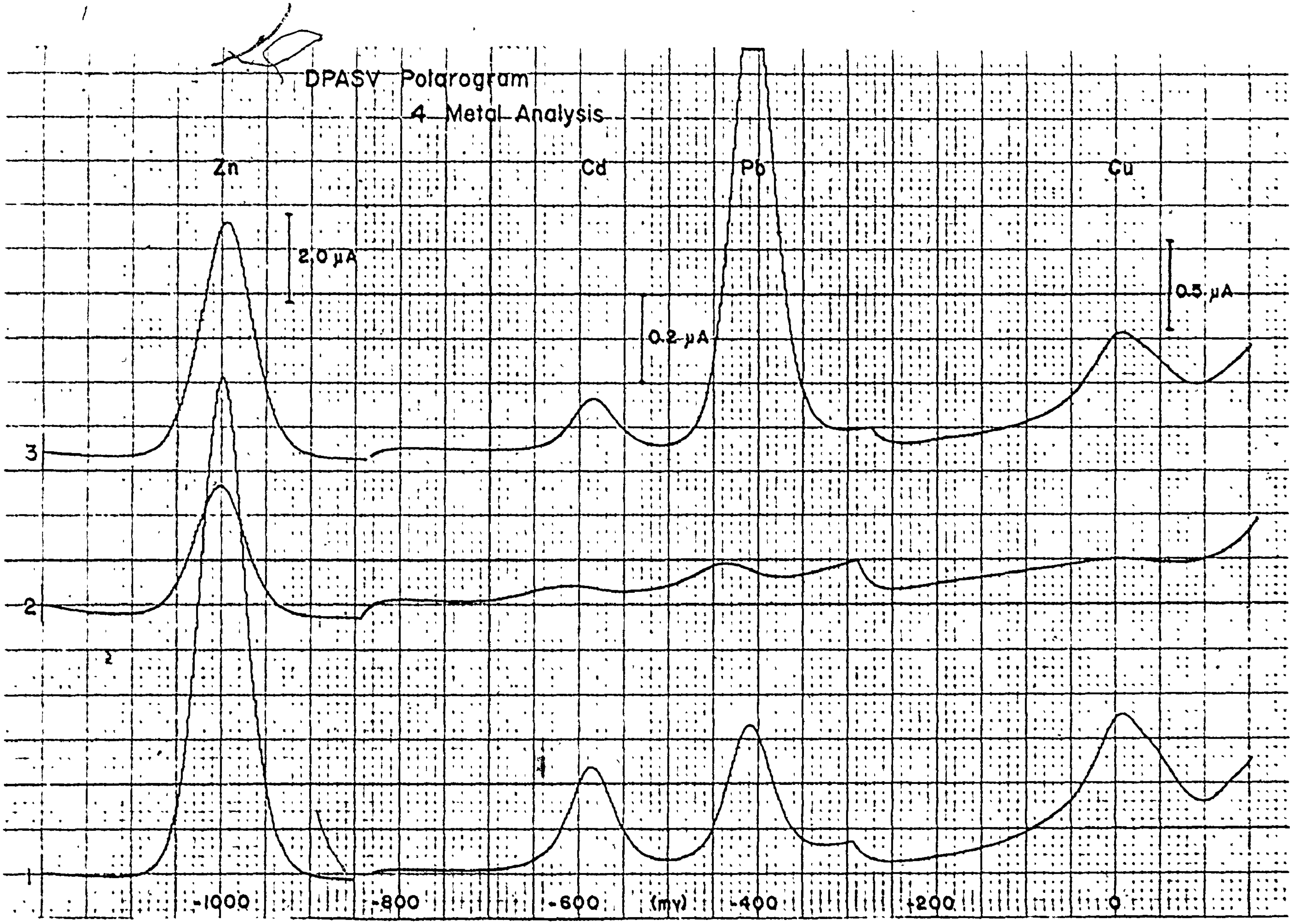

DPASV Polarogram
4 Metal Analysis
Zn
Cd
Pb
Cu
2.0 µA
0.2 µA
0.5 µA
3
2
1
-1000
-800
-600
(mv)
-400
-200
0

FIGURE 17

The Skead sample (Figure 16, No. 1) is of interest. As is usually the case, a labile aquo-Cu^{++} fraction appears with a peak at the correct calibration E_p. There are two additional secondary anodically positioned peaks which are attributed to colloid association as discussed earlier. This effect is more pronounced than usual in this sample and may be the cause of the cathodic shoulder present on the associated Cd peak, although verification of this is impossible.

It should be noted that when plating and stripping initiation have begun at -1200 mV, the principal Cu peak appears at the calibration potential, although the previously discussed anodically shifted peaks (plating at -200 mV) are still represented by either secondary anodic peaks, or else substantial principal peak assymmetry and anodic shouldering. The analytical conditions consequently play an important role in determining the exact polarographic response obtained. It is possible that inclusion of Zn, Cd and Pb plating and stripping influence Cu response by saturating the colloid in the vicinity of the HMDE with these other metals (during stripping, concentrations of these metals are momentarily high in the immediate electrode vicinity), thus altering the subsequent Cu association chemistry. Reduction of strong metal complexes during the plating step is a function of deposition potential, that is, reduction of this potential in effect supplies more energy for complex dissociation, and larger metal peaks are obtained. Analagous interpretation of the Cu peaks obtained in Figures 16 and 17 may be possible, although the anodic peak irregularities attributed to colloids are still obviously present.

III.6.j Metal Speciation

Heavy metal speciation of Ontario precipitation may then be summed up as in Table XIII. Both Hamilton and Northern Ontario figures are given and the results serve to emphasise the importance of pH acting as the "master variable". The "soluble" fraction of Northern Ontario precipitation is 2 to 4 times greater than that of Hamilton. Once again, this must be related to the buffering influence played by the local geology in governing overall precipitation pH and therefore heavy metal chemistry. Areas of predominant silicate rock outcrop must be inherently more environmentally sensitive and vulnerable to changes resulting from "pollution". Reduction in pH of natural water systems is extremely damaging, not only from this factor alone, but also from the much higher levels of soluble toxic metals that are present.

TABLE XIII

AVERAGE PRECIPITATION HEAVY METAL SPECIATION[1] AND CONCENTRATION RANGES[2]

			Cu	Pb	Cd	Zn
Hamilton	Particulate >0.45 μ		83% (0-250 μg/l)	95% (0-4500 μg/l)	66% (0-90 μg/l)	80% (4-4000 μg/l)
	"Soluble"		17% (0-35 μg/l)	5% (0-35 μg/l)	34% (0-33 μg/l)	20% (0-270 μg/l)
Northern Ontario	Particulate >0.45μ		40% (0-160 μg/l)	35% (0-23 μg/l)	17% (0.0-0.5 μg/l)	24% (0-200 μg/l)
	"Soluble"	Colloidally Associated Me^{++}	60% (0-20 μg/l)	0% -	0% -	0% -
		Aquo - Me^{++}	* (20-160 μg/l)	65% (0-27 μg/l)	83% (0.0-2.5 μg/l)	76% (0.2-650 μg/l)

1. Speciation calculated from loading data in combination with ASV results.
2. Species concentration ranges (approximate) indicated in brackets.

* Cu F in excess of $\sim$20 μg/l is present as aquo - Cu^{++} (on average)

IV. SUMMARY

1. Precipitation acts as an excellent mechanism for cleansing the atmosphere of gaseous and particulate contaminants; because of this, it acts as a significant environmental input or cycling mechanism which may have a profound effect in ecologically sensitive (unbuffered) areas.

2. The environmental (toxicological) importance of heavy metals can only be evaluated when their chemical speciation is known.

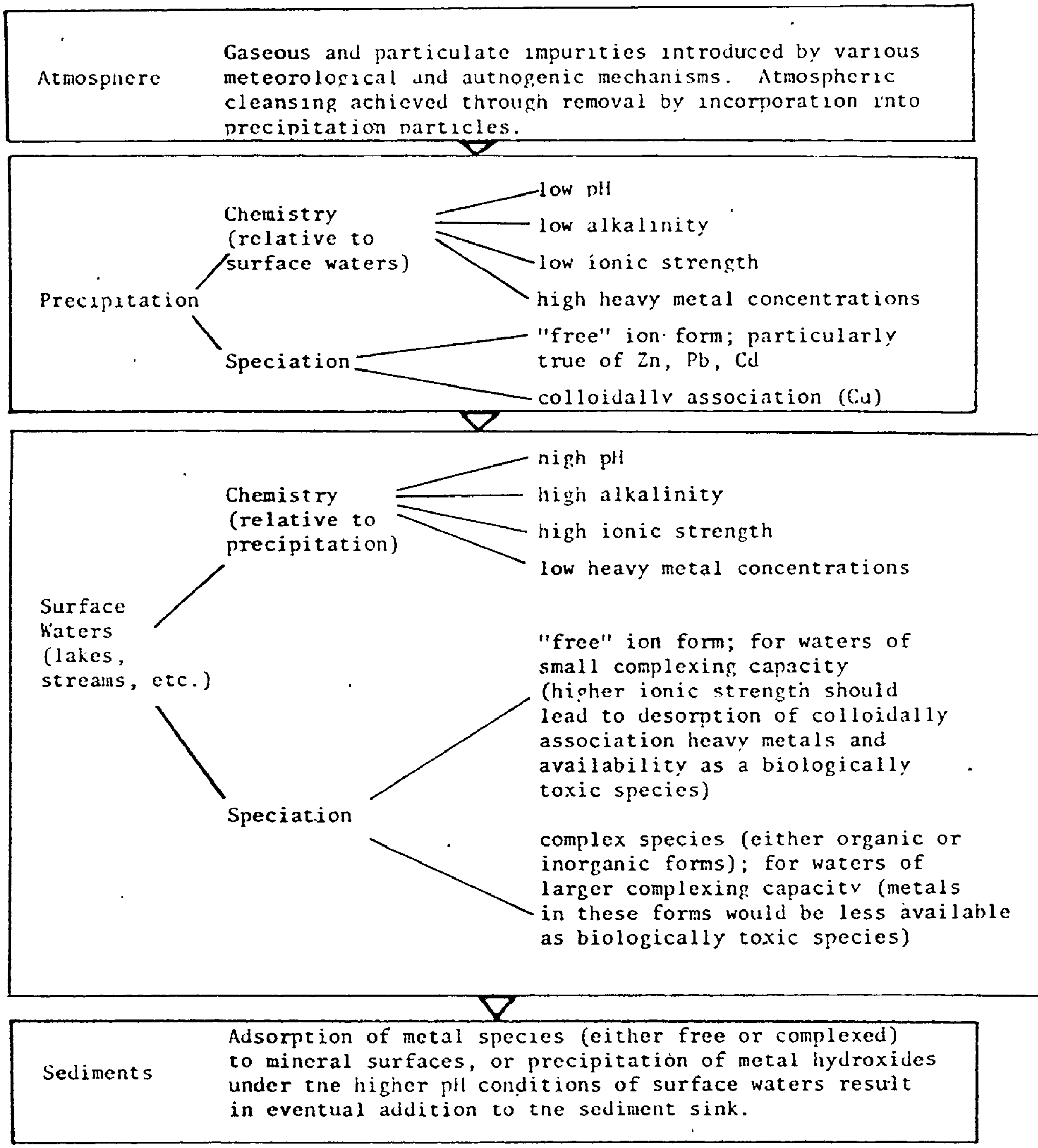
3. Methods capable of species selectivity are insufficiently sensitive to allow for the analysis of most natural samples, <u>except</u> for ASV.

4. Metal speciation of Northern Ontario precipitation using ASV has shown that Cu exists either as the "free" ion when concentrations are sufficiently large to allow this, or else in association with highly dispersed Fe-Mn colloids.

5. When "rained-out" into lakes, colloidally associated metals may become available as toxic agents through desorption processes occurring under the condition of higher ionic strength. (See Figure 18)

6. Continued application of these ASV speciation techniques to other environmental systems is warranted; however, strict control of experimental conditions and a comprehensive understanding of the possible pitfalls is necessary to obtain meaningful results.

7. ASV speciation could find particular utility in experimental metal toxicity studies where all conditions can be rigorously controlled.



Atmosphere

Gaseous and particulate impurities introduced by various meteorological and authogenic mechanisms. Atmospheric cleansing achieved through removal by incorporation into precipitation particles.

Precipitation

Chemistry (relative to surface waters)
- low pH
- low alkalinity
- low ionic strength
- high heavy metal concentrations

Speciation
- "free" ion form; particularly true of Zn, Pb, Cd
- colloidally association (Cu)

Surface Waters (lakes, streams, etc.)

Chemistry (relative to precipitation)
- high pH
- high alkalinity
- high ionic strength
- low heavy metal concentrations

Speciation
- "free" ion form; for waters of small complexing capacity (higher ionic strength should lead to desorption of colloidally association heavy metals and availability as a biologically toxic species)
- complex species (either organic or inorganic forms); for waters of larger complexing capacity (metals in these forms would be less available as biologically toxic species)

Sediments

Adsorption of metal species (either free or complexed) to mineral surfaces, or precipitation of metal hydroxides under the higher pH conditions of surface waters result in eventual addition to the sediment sink.

Figure 18 Box Model Summary of Precipitation Chemistry, Heavy Metal Speciation and Geochemical Cycle.

REFERENCES

Allen, H. E. (1974). Ph.D. Thesis, University of Michigan.

________, W. R. Matson and K. H. Mancy (1970). Trace Metal Characterization in Aquatic Environments by Anodic Stripping Voltammetry. J.W.P.C.F., 42, pp. 573 - 581.

Altshuller, A. P., W. A. Lonneman, F. D. Sutterfield and S. L. Kopczyniski, (1971). Hydrocarbon Composition of the Atmosphere of the Los Angeles Basin - 1967. Environ. Sci. and Tech., 5, No. 10, p. 1009.

Barendrecht, E. (1967). Stripping Voltammetry in Electroanalytical Chemistry, Vol. 2 (A. J. Bard, Ed.). Marcel Dekker, pp. 53 - 109.

Barsdate, R. J. and W. R. Matson (1966). Trace Metals in Arctic and Sub-Arctic Lakes with Reference to the Organic Complexes of Metals in Radioecological Processes (B. Aberg and F. Hungate, Eds.). Pergamon Press, pp. 711 - 719.

________, W. Stumm, J. Hoffman, D. S. Jeffries and R. Huston (1974). EAWAG Communication, Dubendorf, Switzerland.

Beamish, R. J. and H. H. Harvey (1972). Acidification of the La Cloche Mountain Lakes, Ontario, and Resulting Fish Mortalities. J. Fish. Res. Bd. Can., 29, pp. 1131 - 1143.

Bender, M. E., W. R. Matson and R. A. Jordan (1970). On the Significance of the Complexing Agents in Secondary Sewage Effluents. Environ. Sci. and Tech., 4, pp. 520 - 521.

Bradford, W. L. (1973). The Determination of a Stability Constant for the Aqueous Complex $Zn(OH)_2^0$ using Anodic Stripping Voltammetry. Limnol. and Oceanog., 18, No. 5, p. 757.

Brar, S. S., D. M. Nelson, E. L. Kanobrocki, C. E. Moore, C. D. Burnham and D. M. Hattori (1970). Thermal Neutron Activation Analysis of Particulate Matter in Surface Air of the Chicago Metropolitan Area. Environ. Sci. and Tech., 4, No. 1, pp. 50 - 54.

Browning, E. (1961). Toxicity of Industrial Metals. Butterworth and Co. (Canada) Ltd., pp. 126, 150, 223.

Chau, Y. K., R. Gachter and K. Lum-Shue-Chan (1974). The Determination of the Complexing Capacity of Lake Waters. J. Fish. Res. Bd. Can., 13, pp. 1515 - 1519.

——— and K. Lum-Shue-Chan (1974). Determination of Labile and Strongly Bound Metals in Lake Water. Water Res., 8, pp. 383 - 388.

Conroy, N. (1971). Classification of Precambrian Shield Lakes Based on Factors Controlling Biological Activity. M.Sc. Thesis, McMaster University.

———, D. S. Jeffries and J. R. Kramer (1974). Acid Shield Lakes in the Sudbury, Ontario Region. Proc. 9th Canadian Symposium on Water Pollution Research in Canada.

Cotton, F. A. and G. Wilkinson (1966). Advanced Inorganic Chemistry - A Comprehensive Text. Interscience Publishers, p. 895.

Crowther, C. and H. G. Ruston (1911). The Nature and Distribution and Effects upon Vegetation of Atmospheric Impurities In and Near an Industrial Town. J. Agri. Sci., 4, pp. 25 - 55.

Daines, R. H., H. Molto and D. M. Chilko (1970). Atmospheric Lead: Its Relationship to Traffic Volume and Proximity to Highways. Environ. Sci. and Tech., 4, No. 4, p. 318.

Davie, R. F. (1974). The Geochemistry of Streams and Weathering Processes in an Arctic Carbonate Terrain: Cornwallis Island and Grinnell Peninsula Northwest Territories. B.Sc. Thesis, McMaster University.

Engelmann, R. J. (1971). Scavenging Prediction Using Ratios of Concentration in Air and Precipitation. J. Appl. Meteorol., 10, No. 3, pp. 493 - 497.

Flato, J. B. (1972). The Renaissance in Polarographic and Voltammetric Analysis. Anal. Chem., 44, No. 11, pp. 75A - 87A.

Gardiner, J. (1974). The Chemistry of Cd in Natural Waters. I - A Study of Cd Complex Formation using the Cd Specific Ion Electrode. Water Res., 8, pp. 23 - 30.

Greenfield, S. M. (1957). Rain Scavenging of Radioactive Particulate Matter from the Atmosphere. J. Met., 14, pp. 115 - 125.

Grob, K. and G. Grob (1971). Gas-liquid Chromatography - Mass Spectroscopy Investigation of C_6 - C_{20} Organic Compounds in Urban Air. J. Chromatog., 62, pp. 1 - 13.

Guy, R. D., C. L. Chakrabarti and L. L. Schramm (1975). The Application of a Simple Model of Natural Waters to Metal Fixation in Particulate Matter. Can. J. Chem., 53, p. 661.

Hallsworth, E. G. and W. A. Adams (1973). The Heavy Metal Content of Rainfall in the East Midlands. Environ. Poll., 4, No. 3, p. 231.

Handa, B. K. (1969). Chemical Composition of Monsoon Rains Over Calcutta. Part.I. Tellus, 21, No. 1, p. 95.

Harrison, P. R., J. W. Winchester (1971a). Area-wide Distribution of Pb, Cu and Cd in Air Particulates from Chicago and Northwest Indiana. Atmos. Environ., 5, pp. 863 - 880.

________, K. A. Rahn, R. Dams, J. A. Robbins, J. W. Winchester, S. S. Brar and D. M. Nelson (1971b). Area-wide Trace Metal Concentrations Measured by Neutron Activation Analysis. A.P.C.A. Journal, 21, No. 9, pp. 563 - 570.

Hume, D. N. and J. N. Carter (1972). Characteristics of the Mercury Coated Graphite Electrode in Anodic Stripping Voltammetry: Application to the Study of Trace Metals in Environmental Systems. Chema Analityczna, 17, p. 747.

Jeffries, D. S. (1974). The Metal Adsorption Chemistry of Buserite. Unpublished manuscript.

Junge, C. E. (1963). Air Chemistry and Radioactivity. Academic Press, Publisher.

Kamp-Nielsen, L. (1972). Some Comments on the Determination of Copper Fractions in Natural Waters. Deep-Sea Res., 19, pp. 899 - 902.

Kneys, T. J., M. Eisenbud, C. D. Strehlow and P. C. Freudenthal (1970). Airborne Particulates in New York City. J. Air Poll. Control Assoc., 20, No. 3, pp. 144 - 149.

Kolthoff, I. M. and J. J. Lingaine (1952). Polarography, Volume I. Interscience Publishers.

Kortzeborn, R. N. and F. F. Abraham (1970). Scavenging of Aerosols by Rain: A Numerical Study in Precipitation Scavenging, U. S. Atomic Energy Comm. Symposium Series, p. 433.

Koryta, J. (1962). Polarography of Complex Compounds in Progress in Polarography, Vol. I (P. Zuman and I. M. Kolthoff, Eds.). Wiley Interscience, pp. 157 - 194.

Kramer, J. R. (1973). Fate of Atmospheric Sulphur Dioxide and Related Substances as Indicated by Chemistry of Precipitation. Dept. of Geology, McMaster University. Report to Air Management Branch, Ontario Ministry of the Environment.

Kramer, J. R. (1975). Fate of Atmospheric Sulphur Dioxide and Related Substances as Indicated by Chemistry of Precipitation. Dept. of Geology, McMaster University. Continuing report to Air Management Branch, Ontario Ministry of the Environment.

Kramer, J. R. and W. R. Snyder (1974). Precipitation Scavenging of Sulphur Dioxide Using Stable Sulphur Isotopes. Accepted for publication in Precipitation Scavenging (1974), proceedings of U.S. Atomic Energy Commission Symposium on Precipitation Scavenging, 1974.

Krause, M. S., Jr., and L. Ramaley (1969). Analytical Applications of Square Wave Voltammetry. Anal. Chem., 41, p. 1365.

Lao, R. C., R. S. Thomas, H. Oja and L. Dubois (1973). Application of GC-MS-Data Processor Combination to the Analysis of Polycyclic Hydrocarbon Content of Airborne Pollutants. Anal. Chem., 45, No. 6, p. 908.

Lazrus, A. L., E. Lorange and J. P. Lodge; Jr. (1970). Lead and Other Metals in U. S. Precipitation. Environ. Sci. and Tech., 2, No. 4, pp. 288 - 290.

Lee, R. E., Jr., R. K. Patterson and J. Wagman (1968). Particle Size Distribution of Metal Components in Urban Air. Environ. Sci. and Tech., 2, No. 4, pp. 288 - 290.

Lengweiler, H., W. Buser and W. Feitknecht (1961). Die Ermittlung der Löslichkeit von Eisen(III)-hydroxiden mit ^{59}Fe(II), Fallungs und Auflösungsversuche. Helv. Chim. Acta, 44, p. 796.

Likens, G. E., F. H. Bormaan and N. M. Johnson (1972). Acid Rain. Environment, 14, No. 2, p. 33.

Makhon'ko, K. P. (1967). Simplified Theoretical Notion of Contaminant Removal by Precipitation from the Atmosphere. Tellus, 19, No. 3, p. 467.

Martens, C. S. and R. C. Harriss (1973). Chemistry of Aerosols, Cloud Droplets and Rain in the Puerto Rica Marine Atmosphere. J. Geophys. Res., 78, No. 6, p. 949.

Matson, W. R. (1968). Trace Metals, Equilibrium and Kinetics of Trace Metal Complexes in Natural Media. Ph.D. Thesis, Massachusetts Institute of Technology.

Miller, M. S., S. K. Friedlander and G. M. Hidy (1972). A Chemical Element Balance for the Pasadena Aerosol in Aerosols and Atmospheric Chemistry (G. M. Hidy, Ed.). Academic Press, pp. 301 - 312.

Mocken, H. H. and J. J. M. Alderhout (1963). The Relationship Between Concentration of World-wide Fall-out in Air and Rain. Air Water Poll. Int. J., 7, pp. 91 - 93.

Morgan, J. J. and W. Stumm (1964). Colloid Chemical Properties of Manganese Dioxide. J. Colloid. Sci., 19, p. 317.

Morrow, N. L. and R. S. Brief (1971). Elemental Composition of Suspended Particulate Matter in Metropolitan New York. Environ. Sci. and Tech., 5, No. 9, p. 786.

Mrose, H. (1966). Measurements of pH and Chemical Analysis of Rain-, Snow-, and Fog-water. Tellus, 18, No. 2, pp. 266 - 270.

Muller, E. F. and J. R. Kramer (1974). Precipitation Scavenging in Central and Northern Ontario. Presented at the U.S. Atomic Energy Commission Precipitation Scavenging Conference, 1974.

Murray, J. W. (1973). Ph.D. Thesis, Massachusetts Institute of Technology and Woods Hole Oceanographic Institute.

Murray, D. J., T. W. Healy and D. W. Fuerstenau (1968). The Adsorption of Aqueous Metal on Colloidal Hydrous Manganese Oxide in Adsorption from Aqueous Solution (R. F. Gould, Ed.), Advances in Chemistry Series 79, Amer. Chem. Soc.

Oden, S. (1971). Nederbordens forsurning-et generellt hot mot ekoststamen, in Kapital 3: Forurensing av Biologisk Miljovern (I. Mysterud, Ed.) pp. 63 - 98.

Osterberg, R. (1974). Metal Ion-Protein Interactions in Solution in Metals Ions in Biological Systems, Vol. 3 (H. Sigel, Ed.). Marcel Dekker, pp. 45 - 88.

Perone, S. P. and J. R. Birk (1965). Application of Derivative Techniques to Anodic Stripping Voltammetry. Anal. Chem., 37, p. 9.

Postma, A. K. (1970). The Effect of Solubilities of Gases on their Scavenging by Raindrops in Precipitation Scavenging, U.S. Atomic Energy Commission Symposium Series.

Reilley, C. N. and W. Stumm (1962). Progress in Polarography, Vol. I (P. Zuman and I. M. Kolthoff, Eds.). Wiley Interscience, pp. 81 - 121.

Selenzneva, E. S. (1972). Estimation of the Background Contamination of the Atmosphere from the Chemical Composition of Precipitation. Tellus, 24, No. 2, p. 120.

Semkin, R. G. (1975). A Limnogeochemical Study of Sudbury Area Lakes. M.Sc. Thesis, McMaster University.

Shain, I., J. Lewinson (1961). Anal. Chem., 33, pp. 187 - 189.

Shuman, M. S. and G. P. Woodward, Jr. (1973). Chemical Constants of Metal Complexes from a Complexometric Titration followed with Anodic Stripping Voltammetry. Anal. Chem., 45, No. 12, p. 2032.

Sidle, A. B. (1967). Amino Acid Content of Atmospheric Precipitation. Tellus, 19, No. 1, p. 128.

Siegerman, H. and G. O'Dom (1972). Differential Pulse Anodic Stripping of Trace Metals. Amer. Laboratory, 4, No. 6, pp. 59 - 68.

Stiff, M. J. (1971). The Chemical States of Copper in Polluted Fresh Water and a Scheme of Analysis to Differentiate Them. Water Res., 5, pp. 585 - 599.

Strickland, J. D. and T. R. Parsons (1967). A Practical Handbook of Seawater Analysis. Bull Fish. Res. Bd. Can., 167, pp. 115 - 119.

Stumm, W. and H. Bilenski (1973). Trace Metals in Natural Waters: Difficulties of Interpretation Arising from Our Ignorance on Their Speciation in Advances in Water Pollution Research. Pergamon Press, pp. 39 - 49.

Stumm, W. and P. A. Brauner (1973). Chemical Speciation in Chemical Oceanography (J. P. Riley, G. Skirrow, Eds). Academic Press (in press).

Stumm, W. and C. R. O'Melia (1968). J. Amer. Water Works Assoc., 66, p. 514.

Stumm, W. and J. J. Morgan (1970). Aquatic Chemistry. Wiley Interscience, Publisher.

Summer, P. W. and B. Hitchon (1971). Source and Budget of SO_4 in Precipitation from Central Alberta, Canada. Research Council of Alberta Publication 71-AP-16.

Tamamushi, R. and G. P. Sato (1972). Application of Polarography and Related Electrochemical Methods to the Study of Labile Complexes in Solution in Progress in Polarography, Vol. III (P. Zuman, L. Meites and I. M. Kolthoff, Eds). Wiley Interscience, pp. 1 - 72.

Ter Hoar, G. L., R. B. Holtzman and H. F. Lucas, Jr. (1967). Pb and Pb^{210} in Rainwater. Nature, 215, p. 353.

Traversey, W. J. (1971). Methods for Chemical Analysis of Waters and Wastewaters. Publication of Dept. of Fish. and Forest., Water Qual. Div., Inland Waters Br., Ottawa, Ontario.

Van den Berg, C. M. G. (1975) Application of Hydrous Manganese IV Oxide for the Removal of Heavy Metals from Water and Waste. Unpublished manuscript, EAWAG, Dubendorf, Switzerland.

Van der Westhuizen, M. (1969). Radioactive Nuclear Bomb Fall-out: A Relationship Between Deposition, Air Concentration and Rainfall. Atmos. Environ., 3, pp. 241 - 248.

Whelpdale, D. M. (1972). The Contribution of Airborne Pollutants to the Pollution of Large Bodies of Water. Atmosphere, 10, No. 1, p. 18.

Winchester, J. W. and G. D. Nifong (1971). Water Pollution in Lake Michigan by Trace Elements from Pollution Aerosol Fallout. Water, Air and Soil Poll., 1, pp. 50 - 64.

Yoshitaka, K., H. Masahiro and T. Kenzaburo (1970). Distribution of Pb in the Air near City Roads. Keio J. of Med., 19, p. 183.

APPENDIX I

Precipitation Analysis

Samples received at McMaster are analyzed as shown by the schematic shown in Figure 2. The minimum volume required for all the analyses is approximately 700 ml; however, in the event of insufficient volume, the following parameter priority has been established.

1) Cl, conductivity, pH, SO_4
2) P-T, P-TF
3) NH_3-R, NO_2-NO_3-F
4) SiO_2-F
5) CaF, MgF, NaF, KF
6) TKN
7) CuF, FeF, NiF, PbF, CdF, ZnF
8) TKN-F
9) CuT, FeT, NiT, PbT, CdT, ZnT
10) Alkalinity
11) Others

The first five priority items may be handled when sample volume is 200 ml or greater. In addition to measurement of the above, a visual inspection of each sample is made, and a record kept of any macro-contaminants (pine needles, leaves, algae, insects, etc.) that are present.

This information has proved extremely useful in assessing the observed precipitation chemistry, taken in context with possible local contamination effects.

Analytical Techniques

i) Specific Conductivity - measured using an Electronic Switchgear (London) Ltd. conductivity meter (resistance balance type); meter calibration is periodically checked using KCl conductivity standards.

ii) pH, Cl, Fl, Br - measured simultaneously using glass (pH) and solid state selective ion electrodes (halides) versus a gel-type reference electrode in combination with an Orion, Model 801 digital pH meter and Model 855, automatic electrode switch. All samples and standards are stirred throughout the analysis.

iii) Total Particulates - measured by filtering 200 ml of homogenized sample through a pre-treated (acid, H_2O washed), dried (40°C) and pre-weighed Millipore 0.45μ membrane. After re-drying, weighing, particulate weight (g/l) is calculated by difference.

iv) Soluble (filtered) heavy metals - the filtrate from (iii) is analyzed by atomic absorption for Cd, Cu, Fe, Pb, Ni, Zn, using a solvent extraction preconcentration step as follows:

(a) the sample is transferred to a 250 ml separatory funnel, and 10 ml of sodium acetate-acetic acid buffer (pH 4.75) added. (Buffer = 451 g $NaC_2H_3O_2 \cdot 3H_2O$, 1l H_2O, plus sufficient glacial acetic acid to obtain pH = 4.75 and diluted to 2 litres; buffer purification obtained through a dithizone-CCl_4 extraction of heavy metals.)

(b) 10 ml of 1% ammonium pyrrolidine dithiocarbamate (APDC) and 15 ml methyl isobutylketone (MIBK) are added, and the mixture shaken for 5 minutes.

(c) After allowing phase separation (10 minutes), the aqueous layer is discarded and the organic layer placed in a centrifuge vial.

(d) Centrifuging at 1000 rpm for 10 minutes is followed (within 2 hours) by AA analysis using a Jarrel-Ash Atomic Absorption Spectrophotometer.

(e) Suitable aqueous standards and blanks are carried through the analysis.

(f) All glassware is aged and acid cleansed to reduce metal adsorption and used only for this analysis type.

v) Total Heavy Metals - 200 ml of stirred and shaken sample is taken and subjected to a two-stage acid digestion procedure:

(a) 6 ml of concentrated HNO_3 and 1 ml of concentrated $HClO_4$ are added and the sample digested to a few millilitres, followed by cooling.

(b) 3 ml of additional HNO_3 is added and digestion continued down to 1 - 2 ml (not to dryness).

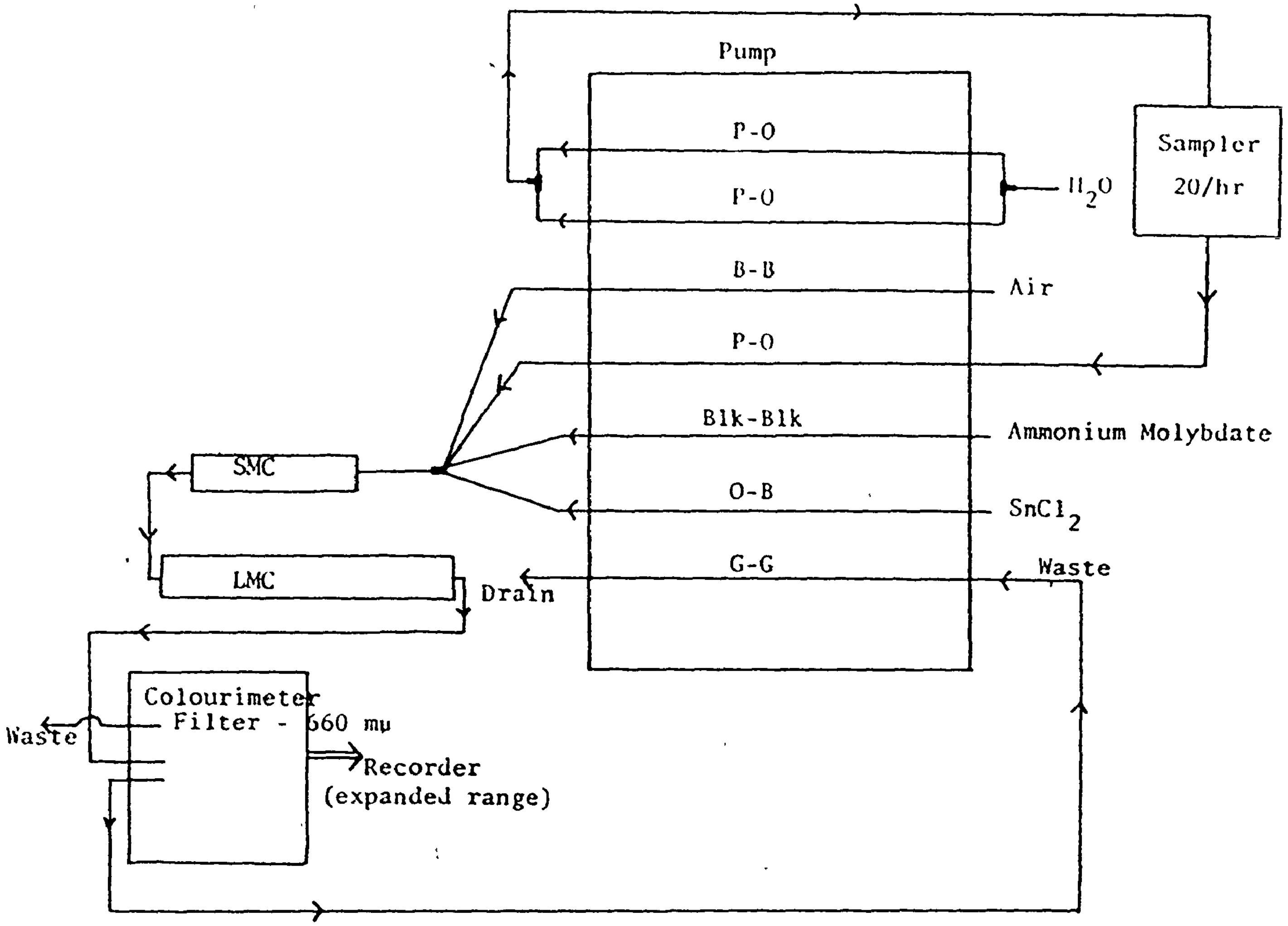
(c) The sample is made back up to 200 ml with deionized water, filtered if necessary, and analyzed by the method outlined for filtered metals. (After addition of the buffer, pH is adjusted to 4.75 ± 0.05 using NH_4OH.)

(d) Acid blanks are carried throughout the analysis; only high purity (Aristar-B.D.H.) acids and NH_4OH are used, thereby obtaining sufficiently low level blanks. It has proved necessary to use these reagents since precipitation samples from non-polluted areas commonly have heavy metal concentrations approaching blank values.

vi) Total P - 50 ml of the homogenized sample is taken, 4 ml of 5% potassium persulphate solution, and 0.5 ml 30% H_2SO_4 are added and the mixture digested to white fumes; 50 ml of deionized H_2O is then added and the solution analyzed using a Technicon single channel auto-analyzer. The molybdate-$SnCl_2$ method is used, in which orthophosphate reacts with ammonium molybdate to form heteropolymolybdophophoric acid, followed by reduction with $SnCl_2$ in H_2SO_4 medium. The molybdenum blue colour obtained is proportional to the P concentration, and colour development is measured in a colourimeter at 660 mμ wavelength. (See P manifold schematic, Figure AI-1.)

vii) Total Filtered P - 50 ml of GFC filtered sample is handled in the same way as for Total P.

viii) SO_4 - After passing two 25 ml portions of filtered (GFC) sample through a freshly regenerated ion exchange column (medium porosity, strong acid type) and discarding, a further 50 ml portion is treated similarly and kept for analysis. Analysis is achieved by titrating the SO_4 against standardized $BaCl_2$ solution (0.4 g $BaCl_2 \cdot 2H_2O$ per litre) using a thorin indicator. Detection



Ammonium Molybdate Solution - 25 g ammonium molybdate + 155 ml conc. H_2SO_4/1 H_2O

$SnCl_2$ - a) Stock $SnCl_2$ - 0.30 g $SnCl_2$ + 25 ml HCl conc.
b) Working $SnCl_2$ - 5 ml stock $SnCl_2$ diluted to 100 ml.

Figure AI-1 Auto-analyzer manifold for PO_4 Analysis

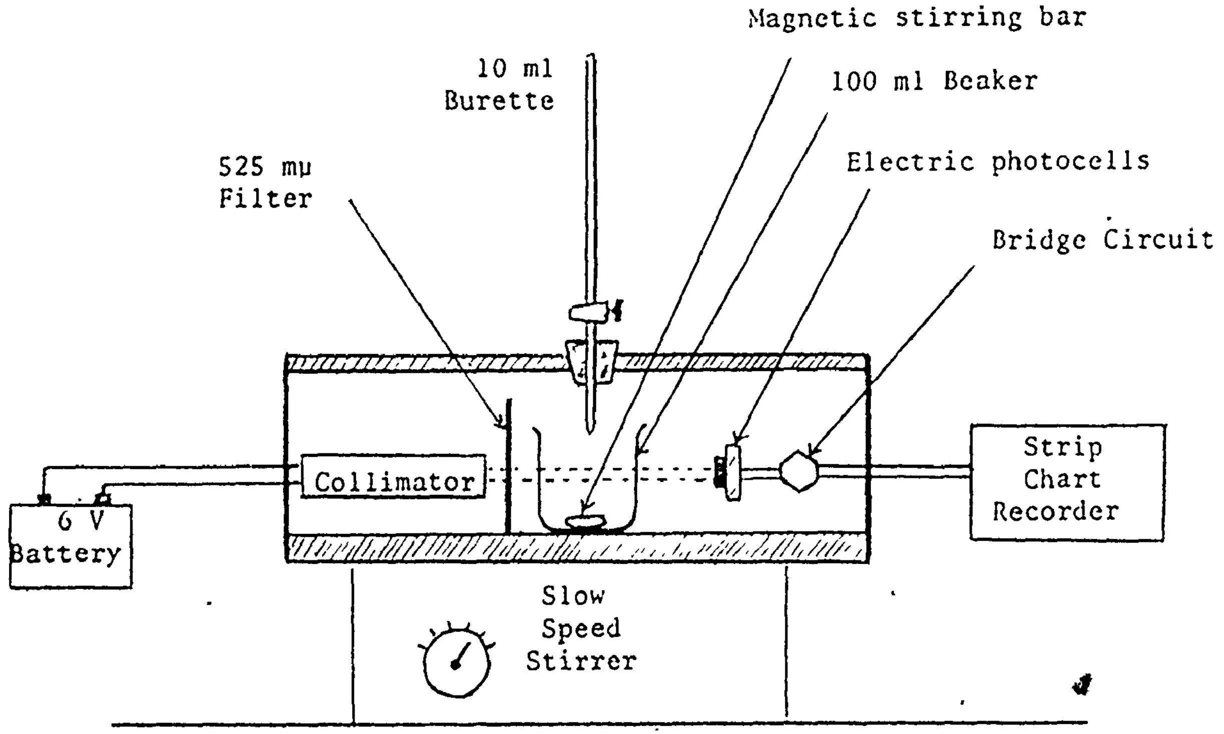


FIGURE AI-2

Schematic of $SO_4^=$ titration colorimeter. Light intensity (525 mμ) is measured using a pair of photocells; output is fed through a bridge circuit and the resultant potential displayed on the recorder. Endpoint (minus blank) is signaled by a sharp change in the slope of the recorder.

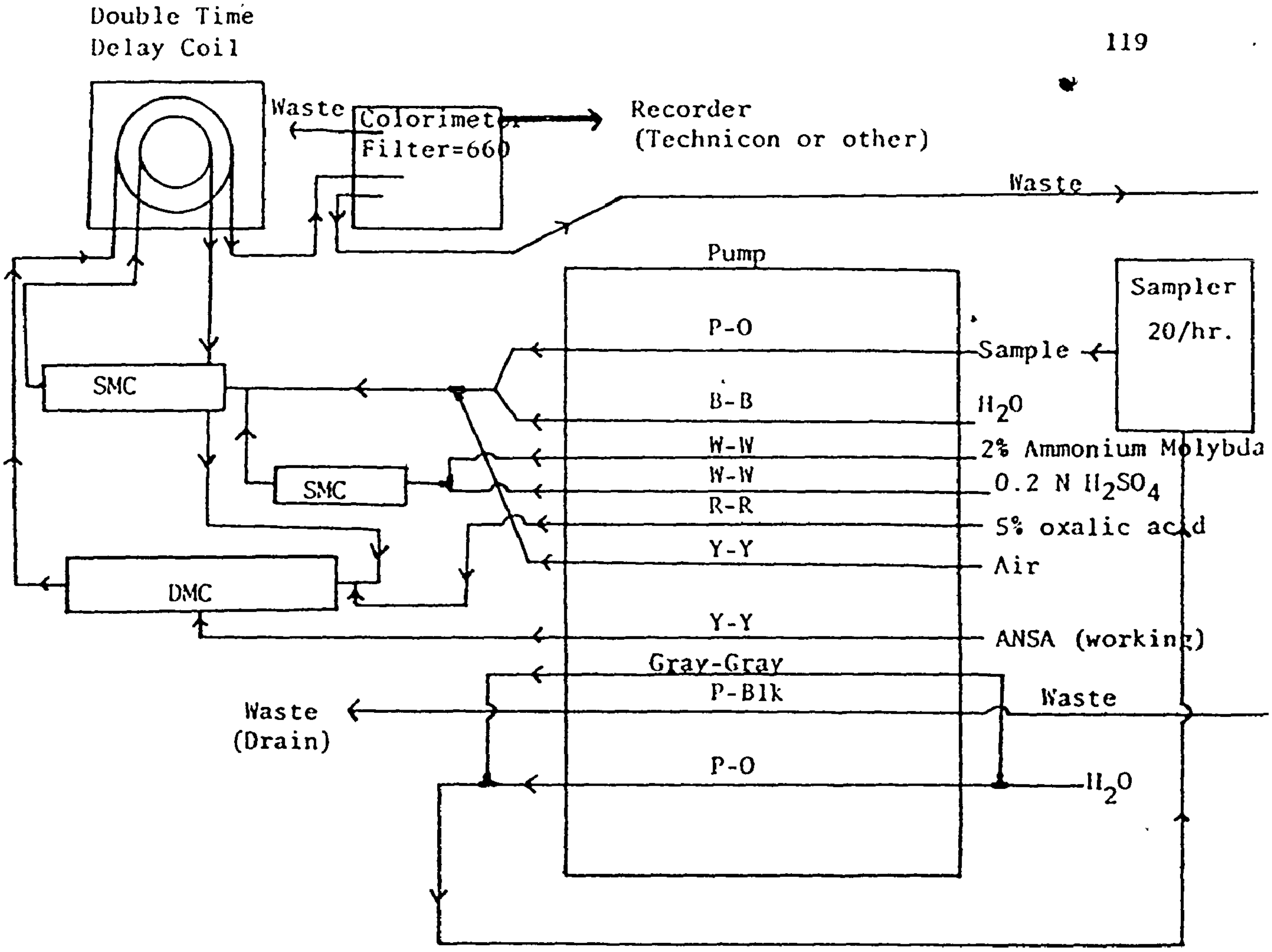
of the endpoint colour change is aided through use of a specially built titration colourimeter (Figure AI-2).

ix) Na, K - measured by atomic absorption on GFC filtered sample using appropriate standards and blanks.

x) Ca, Mg - 10 ml of GFC filtered sample is taken and 50 μl of 10% Sr solution (152 g $SrCl_2 \cdot 6H_2O$/500 ml) is added (optical buffer); analysis achieved by atomic absorption using appropriate standards and blanks.

xi) NO_2 - NO_3 - measured using a Technicon (AAI) auto-analyzer and the standard Cd-reduction method. All nitrate in the GFC filtered sample is reduced to nitrite by placing it in contact with Cd filings; this reproducibility reacts with sulphanilamide to form the diazo compound and the addition of naphthylethylene diamine dihydrochloride results in the formation of the pink azo dye. Colour intensity is proportional to the nitrite concentration and is measured in the filter colourimeter (550 μm). (See NO_2-NO_3 manifold schematic, Figure AI-3.)

xii) NH_3 - ammonia is determined by measuring the colour development of the indophenol complex at 660 mμ (Technicon AAI system). Phenol, ammonia, and hypochlorite react in alkaline solution to produce the blue colour measured. (See NH_3 manifold schematic, Figure AI-4.) Note that for both NO_2-NO_3 and NH_3, the concentration normally encountered in precipitation samples is much higher than that found in many ground and surface water systems. The manifolds have thus been adapted to routinely analyze these



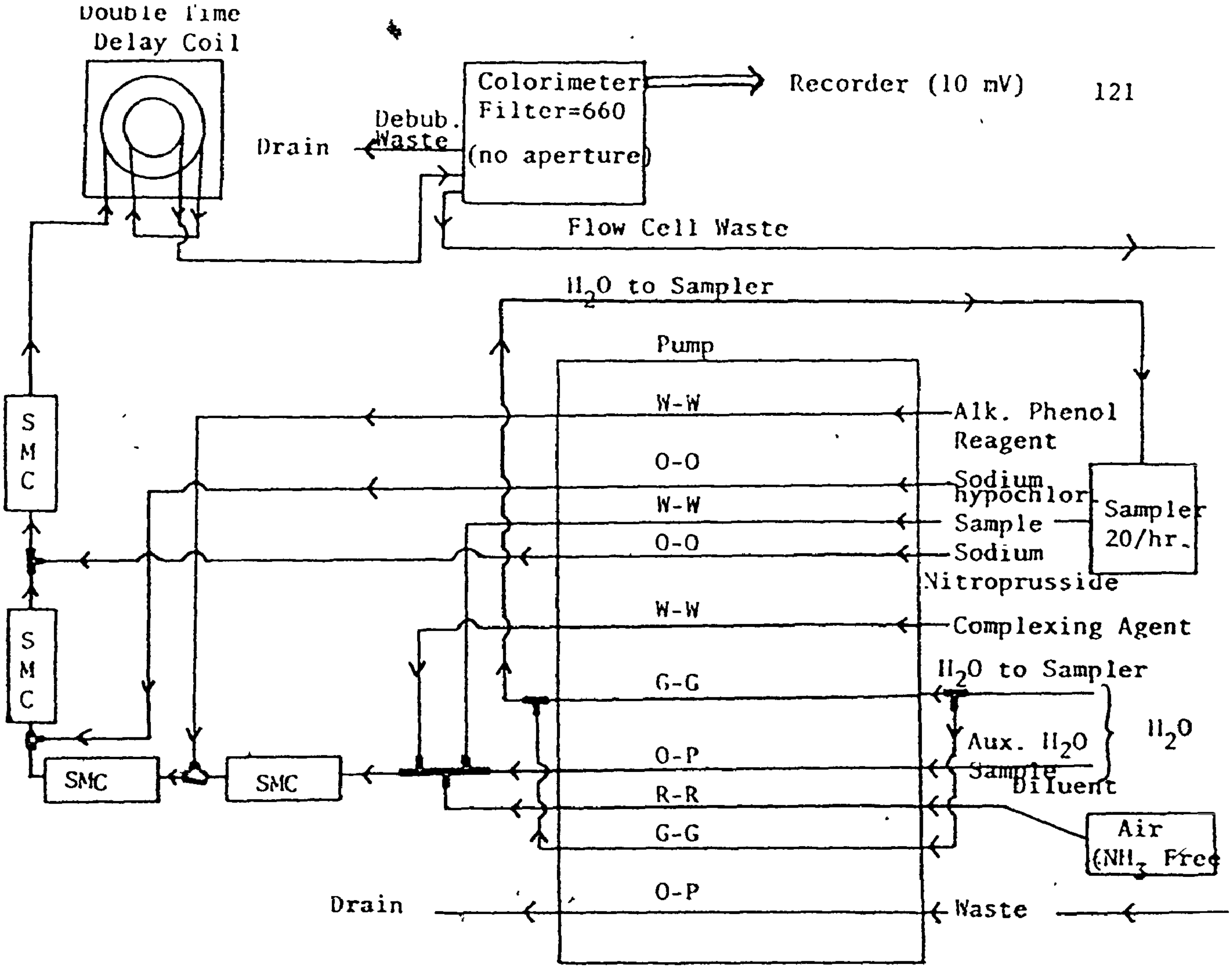
1. 2% Ammonium Molybdate Solution - 20 g ammonium molybdate per litre; filter
2. 0.2 N H_2SO_4 - 11.1 ml H_2SO_4 (conc.) per litre
3. 5% Oxalic Acid - 50 g oxalic acid per litre
4. ANSA Solution - a) Stock solution - 30 g sodium bisulphite + 0.5 g 1-amino-2 napthol-4-sulphonic acid (ANSA) per 250 ml.
   b) Working solution - 100 ml stock ANSA per litre

Figure AI-3 Auto-analyzer Manifold for SiO_2 Analysis.

higher concentrations; for example, the detection limit of the manifold in Figure AI-4 is approximately 10 μg/l NH_3-N.

xiii) <u>SiO_2</u> - measured using the heteropoly blue method. Ammonium molybdate reacts with SiO_2 and PO_4 (pH = 1.2) to produce the heteropoly acids; addition of oxalic acid destroys the molybdophosphoric acid and the remaining molybdosilicic acid is reduced with aminonaphtholsulphonic acid (ANSA) to heteropoly blue. Colour development is proportional to molybdate reactive silica and is measured at 660 mμ (auto-analyzer). (See SiO_2 manifold schematic, Figure AI-5.)

xiv) <u>Alkalinity</u> - measured by titration of a 25 ml GFC filtered sample to a pH of 3.8 with accurate initial and final pH values obtained using a pH meter. Appropriate calculation is then performed to obtain alkalinity in terms of mg/l $CaCO_3$.

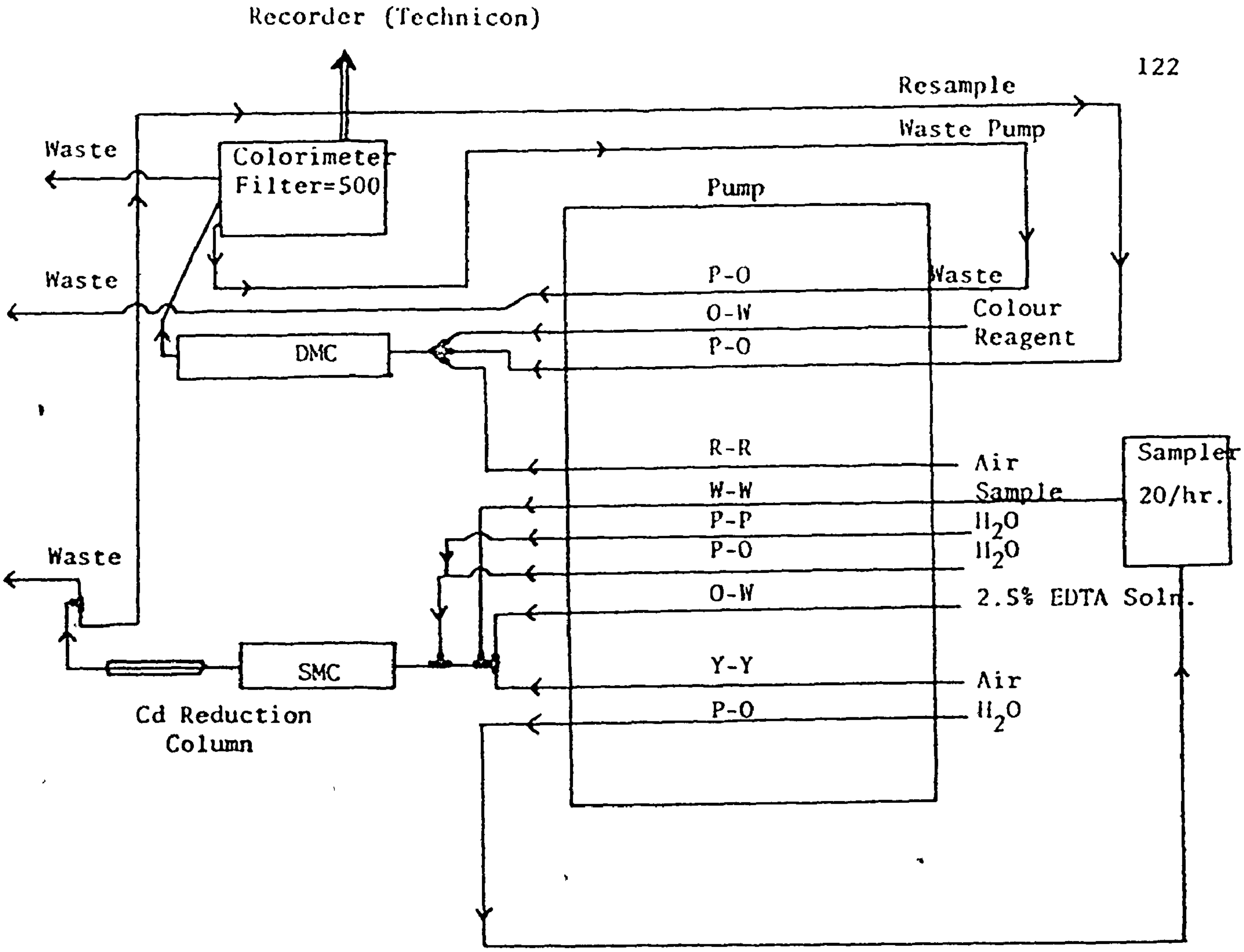


1. Alkali Phenol Reagent - 21 g phenol + 180 ml 5% NaOH per litre

2. Sodium Hypochlorite - 50 ml sodium hypochlorite solution having 5.5% available chlorine per litre

3. Sodium Nitroprusside - 0.25 g sodium nitroprusside per litre

Figure AI-4 Auto-analyzer Manifold for NH_3 Analysis



1. Colour Reagent - 0.2 g Naphthyl Reagent + 1.1 g sulfanilamide + 8.0 ml HCl per 100 ml.

2. 2.5 EDTA Solution - 25 g EDTA per litre plus sufficient 3% NaOH to make pH = 6.5

Figure AI-5. Auto-analyzer manifold for NO_2-NO_3 Analysis

APPENDIX II

Polarographic Reagent and Purification Methods

1. Cu^{++} Standard: 1.0×10^{-3}M Cu^{++} was prepared by dissolving the appropriate weight of the acetate salt (analytical grade) in one litre of aqueous solution and adding a few drops of nitric acid to obtain a pH = 3 ± 0.2; this standard was stable for several months. Standards prepared in the same way from sulphate salts were also used.

2. Supporting Electrolyte/Buffer: 108.42g of sodium acetate trihydrate was dissolved in 190 ml of solution (heating required), followed by the addition of 2.60 ml glacial acetic acid and sufficient water to obtain a final volume of 200 ml. This solution is 4M in acetate and 0.200 ml of this solution per 25 ml sample was found to buffer to 6.0 ± 0.1 when original sample pH fell within the range 4 - 8. Electrolytic purification of this reagent was carried out to minimize blank concentration (see 5).

3. Mercury: Triply distilled Hg was further purified before polarographic use as follows: (adapted from method given by G. C. Whitnach and R. Sasseli, Anal. Chim. Acta <u>47</u>, 267 (1969)
   a) 1 - 2 inches of Hg were placed in an Erlenmeyer flask and covered with a 2-inch layer of high purity 10% NaOH solution; oxygen was vigorously bubbled through the mixture overnight.

b) After decantation and rinsing of the Hg with deionized water, the same process was carried out using 10% HNO_3.

c) Once again decantation was followed by thorough rinsing of the Hg with deionized water, using a separatory funnel.

d) Finally the Hg was dried and any surface residue removed by pin-holing it through Watman #41 filter paper into a suitable storage vessel.

4. All acids and bases used in experiments and analyses were high purity 'Aristar' (BDH) reagents. All glassware and plastic storage bottles were soaked in hot 3M HNO_3, followed by rinsing with deionized water before use in ASV studies. Towards the end of experimentation, addition of a large excess of oxalate was also included in the hot acid wash to ensure complete reduction and removal of any surface-adsorbed Mn and Fe colloids.

5. Purification of the acetate supporting electrolyte/buffer was achieved through controlled potential electrolysis using a vessel constructed at McMaster (see below).

The purification method works on the same principle as the ASV analysis itself; that is, metals in the stirred solution are plated onto the large Hg pool electrode by the application of a sufficiently negative potential to allow reduction (-1.200 V used to ensure removal of Zn, Cd, Pb, Cu). Reduction and removal of the metals from solution to extremely low levels may be achieved by extending the plating period to 24 hours or longer.

After a sufficiently long plating period and while reduction (not stirred) is still going on, some of the purified reagent may be removed through the stopcock. It is important that the reagent remain in contact with all electrodes during removal, since breaking of the circuit and hence removal of the applied negative potential will result in spontaneous oxidation of a portion of the metals in the Hg back into solution and recontamination of the reagent.

The PAR Model 174 polarographic analyzer may be used to provide the reduction potential for purification using the following instrument settings:

Pushbuttons = Initial
Operating Mode = DC
Drop Time = Natural
Output Offset-Low Pass Filter = Off
Display Direction = +
Initial Potential = -1.200 V
Scan Range = 1.5 V
Current Range = 10 mA