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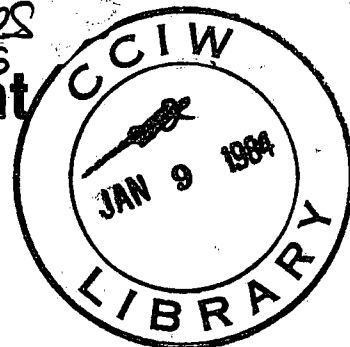
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NWRI. unpublished Manuscript. Numbered Series #83-26



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STUDY ON EFFECTS OF ACID WATER
ON LEACHING OF METALS FROM
DOMESTIC WATER SUPPLIES

BARRINGER MAGENTA LTD.

Contract Report

File # 01SE.KL347-0-1297

Disclaimer

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File # 01SE.KL347-0-1297

For

National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario

Scientific Authorities: Y.K. Chau, P.T.S. Wong and F.C. Elder

March 1983

PREFACE

Water quality deterioration as a result of acid waters in home and building plumbing systems has been a major concern in environmental studies. Although city water supplies are generally treated, rural areas without water treatment facilities may suffer directly from the impact of metal leaching by low pH waters in their water systems.

Studies on corrosion of pipes by water have been related to high oxygen content, low pH and low alkalinity of the water. However, the effects of acidity on metal leaching have not been properly addressed. With the pressing issue of acid precipitation, some basic information on leaching of metals from pipes by acid waters can provide guidance for environmental protection for areas directly under the impact of acid rain. It is the intention of this study to carry out a laboratory investigation and a field survey in Metropolitan Toronto area to examine such effects.

This report presents the results of a study on the effects of pH, temperature and hardness on the leaching of Pb, Zn, Cu, Ni, Co, As and Cd from copper, lead and galvanized pipes used in domestic water supplies. The work was carried out by Barringer Magenta Limited (Scientific Personnel: A. Murray, C. Vairo, R. Jackson, W. Li) under a contract funded by the Department of Environment, File #01SE.KL-47-0-1297, in 1981. This report has been made available to National Health and Welfare and to the Ontario Ministry of Environment. Copies are being placed in the library of C.C.I.W. for reference purposes. Appendix material is available in the files of the Environmental Contaminants Division, National Water Research Institute.

Y.K.C.

P.T.S.W.

F.C.E.

March 1983

ABSTRACT

Laboratory studies of the effect of pH, temperature and hardness on the leaching of metals from domestic plumbing materials are completed. The results indicate that significant changes occur in new pipe material during the first few weeks of contact with water. Decreasing pH results in increased rates of leaching of metals, principally lead, copper and zinc, from piping materials. A decrease of pH from 8 to 6 can result in substantial increases in the leaching of lead and copper from the most widely used plumbing material, soldered copper pipes.

The effect of temperature is slight, up to 30°C, for all metals, except lead. No significant difference between soft and hard water was observed at pH 8.0.

A survey of 105 sites in the Toronto area was completed and showed some good correlations with the results of the laboratory study, particularly the effect of a lowering of metal concentrations after flushing the water system compared to levels in standing water. Only lead was found at concentrations higher than the recommended level, at some sites, and then, only in the standing samples. The pH values in all of the samples were essentially the same, as were the hardness levels, and this precludes any statistical analysis of these parameters. The effects of pH, and hardness, on field samples must thus await further survey work.

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1. INTRODUCTION

It is a recognized phenomenon that heavy metal concentration of household water can be increased by contamination from the pipes, fittings and joints used in the household distribution system. One aspect of the effects of acid precipitation is a lowering of the pH of river and lake water which eventually comes in contact with the metals in these household distribution systems. It can be expected that lowering the pH of water will increase the amount of metals leached from domestic pipes, resulting in increased intake of the metals by the consumer and faster corrosion of the plumbing⁽⁷⁾.

In general, experimental studies of the effects of pH, and other parameters such as alkalinity and hardness on the corrosion of pipes have been carried out by public water treatment facilities^(1,2). These studies tend to address problems of process control in the treatment facilities and the economic impact of corrosion of the main distribution systems. High corrosion rates are generally always associated with water of low pH and low hardness^(1,5). A simple measure of the corrosive nature of water used in such studies is the Aggressive Index (A.I.), a measure in which lower numbers indicate more corrosive waters. Very corrosive waters have an A.I. less than 10, and it is estimated that over 16% of the public water facilities in the U.S. handle water of this class⁽⁵⁾.

General surveys of drinking water in Canada and the U.S. have indicated that the levels of heavy metals are well below the recommended maximum limits^(3,4,6). A survey of 969 public water supply systems in the U.S. found that 1% or less of the facilities exceeded recommended values for As, Cu, Zn, Cd and

Pb(3). A national survey (6) of drinking water in Canada found levels of Cd, Cr, Cu, Pb and Zn to be well below the W.H.O. recommended upper limits. The mean values for selected elements are shown in Table 1.1 along with guidelines for acceptable levels in drinking water in Canada.

It should be noted that both of the above-mentioned surveys were carried out on samples taken after flushing the water system for some length of time (usually of the order of several minutes). It is well known that the first water drawn from the tap in the morning shows generally higher levels of a number of elements due to the increased time of contact of the water with the pipes and fixtures in the plumbing system(6).

The metal that has received the greatest attention by investigators has been lead (1, 8-13). The leaching of this metal has been studied extensively in Great Britain where a large part of the population live in older houses equipped with lead pipe and lead-lined storage tanks. A general survey of houses in England, Scotland and Wales (9) found 9% of homes had lead concentrations 0.1 mg/l (W.H.O. recommended limit) and 20% were 0.05 mg/l (Canadian limit) in "first draw" water, while samples taken, during the day, after the system had been flushed were significantly reduced (4% > 0.1 mg/l and 10% > 0.05 mg/l). Other studies (8,10) found 3 to 10 fold decreases in the concentration of lead after flushing the pipes for 2 to 5 minutes.

As could be expected, generally higher levels of lead were found in (9) houses with greater amounts of lead in the plumbing system, but even houses plumbed with copper pipe can show high levels of lead. In Glasgow (11), a city noted for highly corrosive water, due to it's softness and low pH,

TABLE 1.1

Mean Concentrations and Recommended Upper Limits in Drinking Water; Mean Results for Toronto Drinking Water.

Data For Lake Ontario

Element	Mean		Upper Limit ^a	Mean, Toronto		Lake Ontario
	Canada ^d	U.S. ^e		1st Draw	Running	
----- ppb (µg/ℓ) -----						
Cd	<0.1	1.3	10 ^c	0.5	0.9	<0.2-1.4
Co	-	2.2	b	<1	<1	-
Cu	20-75	15 ^f	1000	222	24	0.5-3.0
Pb	<1.0	<1-20 ^g	50 ^c	27	3.9	0.5-1.5
Ni	-	4.8	b	3.9	1.7	0.5-2.0
Zn	≤5	193.8	5000	156	28	1.0-12.0
As	-	-	50 ^c	<1	<1	-

a McNeely, R.N., Naimanis, V.P. and Swyer, L. "Water Quality Source Book", Environment Canada, Ottawa, Ontario, 1979.

b no recommended limit given in (a).

c maximum permissible level.

d Meranger, J.C., Subramanian, K.S. and Chalifoux, C. Environ. Sci. Technol., 13, 707 (1979).

e Craun, G.F. and McCabe, L.J. J. Am. Water Works Assoc., 67, 593 (1975).

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g NAS Lead in the Environment.

tenement apartments with soldered copper plumbing showed an average lead concentration of 0.106 ± 0.023 mg/l in "first draw" water.

In the United States, two areas that have received extensive investigation have been Seattle (1) and Boston (13). Both cities have highly corrosive water which is both soft and quite acidic (hardness 15 mg/l as CaCO_3 , pH in Boston 6.7, Seattle 5.5 (13)). In Seattle (1), studies were carried out to measure the effect of different water treatments on the rates of corrosion and on the leaching of specific elements. The level of Pb found in water that passed through sections of new galvanized pipe were up to .04 mg/l using the normal water supply, but this was decreased to 0.01 mg/l when the water was treated with lime and bicarbonate.

Controlled laboratory tests on leaching of metals from pipes have not been extensive, and have focussed mainly on lead. A study in Britain (12) looked at the leaching of lead from the standard 50/50 lead-tin solder used in copper plumbing. It was found that 200-300 ug of lead was released per joint in newly soldered copper pipe sections in tap water left in the pipe for 16 hr. This dropped to 10-30 ug per joint over a 4-5 week period. Samples removed from sections of pipe in an office building showed more erratic behaviour, which was ascribed to inhomogeneity in the samples. Another study (10) looked at the effect of pH using a 50 year old section of lead pipe and found large increases in the rate of release of Pb at pH values less than 6 or greater than 8. Controlled studies on the release of elements other than lead have been reported with much less frequency (16, 17).

The purpose of one part of this study was to investigate systematically the effect of varying pH on the leaching of

several metals from the three major types of pipe material used in domestic water distribution systems: copper, galvanized steel and lead. Other parameters of interest that were to be varied were the hardness of the water and temperature. Dynamic tests involving sampling under flow conditions and static tests with various durations of contact between the test solutions and pipes were to be carried out to assess both the rate of release of metals and equilibrium effects.

In conjunction with this laboratory study, a survey of tap water samples was to be collected in the metropolitan Toronto area. Both a "first-draw", or standing, sample and a running sample obtained after flushing the system, were to be collected. This survey was to provide data to assess the results of the laboratory study.

2. EXPERIMENTAL

2.1 ANALYTICAL METHODS

pH measurements were done using an Orion Research pH meter (Ionalyser, Model 407A), equipped with a glass pH electrode (Fisher Scientific Ltd., #13-639-3) and a single junction reference electrode (Orion Research, Inc. Model 90-01). Calibration of the pH meter was performed daily using buffer solutions of pH 5, 7 and 9 prepared from Certified Buffer Tablets (Perkin-Elmer Corp.) according to the manufacturers instructions.

Hardness was determined according to the method given in Standard Methods for the Examination of Water and Wastewater (APHA, AWWA and WPCF, 14 ed., page 202, 1975). This is a titrimetric method involving complexation of Ca^{2+} and Mg^{2+} with EDTA at pH 10.0 using Eriochrome Black T as end-point indicator. Most polyvalent cations which normally interfere are complexed by the addition of cyanide.

The concentration of the elements Cd, Co, Cu, Ni, Pb and Zn in the waters were determined in most cases by graphite furnace atomic absorption spectroscopy (G.F.A.A.S.). For some solutions of the laboratory study, the concentration of some metals was so high that flame atomic absorption spectroscopy (F.A.A.) was used. For the G.F.A.A.S. determinations, a Varian AA-475 atomic absorption spectrometer was used. The spectrometer was operated in the double beam mode and absorption measurements, taken in the peak-height mode, were recorded on a strip chart recorder (Hewlett Packard Model 7100B). A summary of the analytical lines, lamp currents and other instrumental settings used is given in Table 2.1.

TABLE 1.1

Mean Concentrations and Recommended Upper Limits in Drinking Water; Mean Results for Toronto Drinking Water.

Data For Lake Ontario

Element	Mean		Upper Limit ^a	Mean, Toronto		Lake Ontario
	Canada ^d	U.S. ^e		1st Draw	Running	
----- ppb (µg/ℓ) -----						
Cd	<0.1	1.3	10 ^c	0.5	0.9	<0.2-1.4
Co	-	2.2	b	<1	<1	-
Cu	20-75	15 ^f	1000	222	24	0.5-3.0
Pb	<1.0	<1-20 ^g	50 ^c	27	3.9	0.5-1.5
Ni	-	4.8	b	3.9	1.7	0.5-2.0
Zn	≤5	193.8	5000	156	28	1.0-12.0
As	-	-	50 ^c	<1	<1	-

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TABLE 1.1

Mean Concentration and Recommended Upper Limits in Drinking Water; Mean Results for Toronto Drinking Water.

Data for Lake Ontario

Element	Mean		Upper Limit ^{a)}	Mean, Toronto		Ontario
	Canada ^{d)}	U.S. ^{e)}		1st Drawn	Running	
----- ppm (mg/L) -----						
Cd	≤0.0001	0.0013	0.01 ^c	0.00055	0.00098	<0.0002-0.0014
Co	-	0.0022	b	<0.001	<0.001	-
Cu	0.020-0.075	0.015 ^f	1.0	0.2229	0.0239	0.0005-0.003
Pb	0.001	0.001-0.020 ^g	0.05 ^c	0.0273	0.0039	0.0005-0.0015
Ni	-	0.0048	b	0.0039	0.0017	0.0005-0.002
Zn	≤0.005	0.1938	5.0	0.1564	0.0276	0.001-0.012
As	-	-	0.05 ^c	<0.001	<0.001	-

a McNeely, R.N., Neimanis, V.P. and Dwyer, L. "Water Quality Source Book", Environment Canada, Ottawa, Ontario, 1979.

b no recommended limit given in (a).

c maximum permissible level.

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TABLE 2.1Instrumental Settings for G.F.A.A.S.

A.A.	Element					
	<u>Cd</u>	<u>Co</u>	<u>Cu</u>	<u>Pb</u>	<u>Ni</u>	<u>Zn</u>
Lamp	_____ HCL _____					
Lamp current, mA	4	10	4	7	10	7
Wavelength, nm	228.8	240.7	324.7	283.3	232.0	213.9
BK/G correction	_____ on _____					
Integration	_____ 10S _____					
Mode	_____ Peak height _____					
<u>Graphite Furnace</u>						
Dry Temp., °C	125	125	125	125	125	125
Time, S	30	30	30	30	30	30
Ash Temp., °C	500	900	900	500	900	400
Time, S	30	30	30	30	30	30
Atomize Temp., °C	1900	2700	2700	2700	2700	2500
Time, S	10	10	10	10	10	10
Purge Gas	_____ Argon _____					
Flow mode	Normal	_____	Interrupt	_____	Normal	

Sample atomization was performed using a Perkin-Elmer Model HGA 2100 graphite atomizer, with pyrolytically coated graphite tubes obtained from the manufacturer. Samples were introduced into the tubes by a Perkin-Elmer AS-1 automatic sampler, equipped with 2.5 ml disposable polystyrene sample cups. The sample size was 20 ul. The operating parameters for the furnace are given in Table 2.1. The detailed analytical procedures, based on those of USEPA (1979), are given in Appendix B.

For some of the laboratory study solutions, FAA determinations of Cu and Zn were performed using a Varian Techtron AA-5 spectrometer. The hollow cathode lamp lines and analytical wavelengths were the same as given for these elements in Table 2.1. Flame and other instrumental settings were those recommended by the manufacturer.

The determination of As was by heated quartz tube atomic absorption spectroscopy. The As is volatilized by converting it to AsH_3 by in-situ reduction of arsenic by the acid-induced decomposition of $NaBH_4$. The method is semi-automatic and the sampling and hydride generation train is based on that of Vijan et al (20). The analytical wavelength and detection limits for the metals, based on 20 ul sample size, are given in Table 2.2.

2.2 LABORATORY STUDY OF LEACHING OF METALS FROM DOMESTIC PIPES

Three different pipe materials were used for the laboratory study, namely copper, galvanized and lead pipe. Fifty foot lengths of each material was used, and two lengths of each type of pipe were prepared.

TABLE 2.2

Detection Limits for Metals by Graphite Furnace
Atomic Absorption Spectroscopy

<u>Metal</u>	<u>Analytical Wavelength</u> (nm)	<u>Detection Limit</u> (ppb)
Cd	228.8	0.5
Co.	240.7	1
Cu	324.7	1
Pb	283.3	1
Ni	232.0	1
Zn	213.9	0.5
As*	193.7	1

* Determined by heated-quartz tube A.A. with hydride generation.

The copper pipe used was the nominally 1/2" i.d. thin-walled hard copper pipe normally used in domestic plumbing applications, obtained from a commercial plumbing outlet in Toronto. The pipe was cut into 35" sections which were formed into a square coil of fifty feet total length using 90° copper elbow joints. The joints were soldered by a commercial plumber with the 50/50 Sn/Pb solder normally used. Tubes used to introduce and remove test solutions were attached to the ends of the coil using short (2") lengths of 1/2" i.d. tygon tubing which made a leak-tight fit around the outside of the copper tube.

Galvanized steel pipe, nominally 1/2" i.d., was also of the type normally used in plumbing applications. It was cut into 35 and 41" sections to form a rectangular coil. The ends of the pipe were threaded using a commercial pipe-threading machine and the pipe lengths degreased by washing with detergent. The connections to the threaded, 90° galvanized steel elbows used to form the coil were sealed by using teflon tape. Connections to tubing for sample introduction were made using galvanized steel hose connectors that screwed into elbow joints at each end of the coil.

Used lead pipe proved impossible to obtain inside the time limit imposed by the termination date of the contract. It became necessary to purchase new pipe directly from the manufacturer. Two 50 ft. coils of pipe, 1/2" i.d. x 29/32" o.d. were obtained from Lyman Plumbing, Downsview, Ontario. The pipe was delivered and used as circular coils, 3 feet in diameter. Connection to delivery tubing was by polypropylene hose-fittings held in place by teflon tape.

Before any experimentation, all of the prepared pipe coils were

cleaned by pumping a diluted soap solution through them for several hours, followed by a thorough rinse using tap water and finally a rinse using distilled, de-ionized water.

Sample solutions were pumped through the test pipes using a rotary peristaltic pump (Masterflex Model 7545-00, Cole-Parmer Instrument Co., Chicago) at a rate of 1 l/min. Teflon tubing, 1/4" o.d., was used to connect the tygon tubing in the pump to a short section of tygon tubing on the fittings at the end of each pipe. Blank solutions were obtained from the end of the teflon tube that would be connected to the test pipe for each test solution and each pipe material.

Test solutions were prepared in a 25 l polypropylene carboy. The hard water test solutions used the municipal tap water supply at B.M.L., which has a hardness of 137 ± 3 mg/l CaCO_3 as measured several times. The pH was adjusted using NaOH (Baker, Reagent Grade) or H_2SO_4 (BDH, Analytical Grade, concentrated). Soft water, similar in composition to the artificial soft water prepared by Sylva (19), was prepared using distilled, de-ionized water and reagent grade salts to yield the concentrations of various cations and anions given in Table 2.3. The hardness of this water is 22.4 mg/l CaCO_3 equivalent.

Dynamic tests were performed by pumping test solution through the pipe at a rate of 1 l/min for 5 minutes, then collecting a 500 ml sample of the solution at the outlet end of the pipe as the solution was pumped through. For static tests, the test solution was pumped through the pipe for 5 minutes, then the pump was stopped and the ends of the test pipe sealed by using pinch clamps on the short tygon pieces connected to the fittings. After the end of the test period, a 500 ml sample was drained from the pipe by gravity.

TABLE 2.3

Composition of Soft Test Water

<u>Ion</u>	<u>Conc, M</u>
Ca^{2+}	1.5×10^{-4}
Mg^{2+}	7.4×10^{-5}
Na^{+}	2.7×10^{-4}
K^{+}	3.6×10^{-5}
Cl^{-}	3.4×10^{-4}
SO_4^{2-}	7.4×10^{-5}
HCO_3^{-}	2.7×10^{-4}

For the tests above and below room temperature, the pipe and carboy containing the test solution were placed into a temperature controlled chamber for several hours before the test. Thus both pipe and solution were at the test temperature throughout the test period. The chamber maintained temperatures of $4 \pm 1^{\circ}\text{C}$ and $30 \pm 1^{\circ}\text{C}$ for the two test temperatures. Ambient temperature studies were performed in an air-conditioned room maintained at $20 \pm 2^{\circ}\text{C}$.

Samples of test solutions for metals analysis were collected in 500 ml screw-top polypropylene bottles that had been previously soaked in 1% HNO_3 overnight and rinsed with distilled, de-ionized water. The samples were acidified directly after collection by the addition of 2.5 ml concentrated HNO_3 (Baker Ultrex grade), and were analyzed as described above for the seven metals.

2.3 SURVEY STUDY

A survey of domestic tap-water supplies was performed with samples supplied almost exclusively by personnel of B.M.L. and Barringer Research Limited. Some samples were collected at institutional sites, including three recently-built office buildings, and several older buildings in downtown Toronto. The majority of the samples were obtained from private residences built since 1944.

For each site, two 500 ml polypropylene screw top bottles (previously washed with nitric acid and rinsed with distilled, de-ionized water) were supplied along with instruction sheets and a questionnaire. An example of the instructions and questionnaire are given in Appendix A. Each participant was requested to take a standing sample of first-draw water by filling one of the bottles with water from the kitchen water tap. This

sample was to be taken as the first water drawn from the house water supply in the morning, and an estimate of the time elapsed since the last previous use of the water system given. A running sample was then to be collected in the second bottle after the faucet had been left running for approximately five minutes. These samples were then delivered to B.M.L., generally on the morning that they were collected.

A 100 ml aliquot was removed from each bottle upon delivery to B.M.L. for pH and hardness determinations. The remaining sample was acidified by the addition of 2 ml of HNO_3 (Baker, Ultrex, concentrated) to preserve it for the metals analysis.

2.4 QUALITY CONTROL

The quality assurance procedure at B.M.L. employs quality control techniques which define background, precision and accuracy. A reagent blank, lab blank, control standard, repeat sample and certified standard are run with a frequency of 10% of total analyses. Since no appropriate certified standard is available, a pool solution containing low levels of the metals of interest was used.

3. RESULTS AND DISCUSSION

3.1 QUALITY ASSURANCE

In order to determine the relative validity of the results, Barringer Magenta Limited (B.M.L.) routinely performs quality control analysis on all research and analytical services. In the the case of analytical results, B.M.L. evaluates the accuracy and precision of the analytical data. In the absence of an absolute reference material for the samples, a pooled solution containing low levels of the metals of interest was used. For this project, a pooled solution containing 1 mg/l of Cu, Pb, Zn, Ni and Co, and 0.5 mg/l of Cd was prepared in B.M.L. tap water which is known to contain very low levels of these metals. This pooled solution was treated as a sample through-out all of the preparation and analysis steps for all samples to evaluate accuracy. Repeat determinations of some samples were done to evaluate precision. These quality control data are presented in Tables 3.1 and 3.2. As can be seen from Table 3.1, the accuracy measured as % recovery was better than 95% for Pb, Zn, Cu, Ni, Co and Cd in the pooled solution. As can be seen from Table 3.2, precision measured as coefficient of variance was less than 10% for all metals studied as well as pH and hardness.

3.2 LABORATORY STUDY

The results of the laboratory tests of the effect of pH, temperature and water hardness, while showing some qualitative trends, tended to be quantitatively erratic. It appears that all of the pipes show effects of aging even during the short duration of these tests, compared to the lifetime of pipes in

QUALITY CONTROL DATA

[illegible]

TABLE 1.2

QUALITY CONTROL DATA

	Pb ppb	Zn ppb	Cu ppb	Ni ppb	Co ppb	As ppb	Cd ppb	pH	Hardness (mg/l CaCO ₃)	
SU 0410-C				1	< 1		< 0.5			
SU 0410-C (RPT)				< 1	< 1		< 0.5			
MT 0520-L	8			2	< 1					
MT 0520-L (RPT)	9			2	< 1					
WE 0330-X								7.35	134	
WE 0330-X (RPT)								7.40	133	
MT 0500-C								7.30	133	
MT 0500-C (RPT)								7.35	134	
RE 0831-C	< 1	3.8		< 1	< 1		< 0.5			
RE 0831-C (RPT)	< 1	2.8		< 1	< 1		< 0.5			
MT 1091-M	48			2	< 1		< 0.5			
MT 1091-M (RPT)	46			2	< 1		< 0.5			
MT 1061-X				< 1	< 1					
MT 1061-X (RPT)				< 1	< 1					
WE 0580-G								7.60	143	
WE 0580-G (RPT)								7.70	141	
MT 1201-G								7.45	140	
MT 1201-G (RPT)								7.45	140	
SC 1241-C		1.3								
SC 1241-C (RPT)		1.3								
MT 1130-G							1.1			
MT 1130-G (RPT)							1.1			
MT 1150-X							4.4			
MT 1150-X (RPT)							4.4			
MT 0990-X							0.5			
MT 0990-X (RPT)							0.9			

QUALITY CONTROL DATA

	Pb ppb	Zn ppb	Cu ppb	Ni ppb	Co ppb	As ppb	Cd ppb	pH	Hardness mg/l CaCO ₃	
MI 0051-G	< 1		7	1	< 1	< 1	< 0.5	7.70	149	
MI 0051-G (RPT)	< 1		7	1	< 1	< 1	< 0.5	7.75	150	
WE 0231-X	6	6.5								
WE 0231-X (RPT)	5	6.9								
SC 0341-C	3	0.8	10							
SC 0341-C (RPT)	3	1.0	8							
MI 0471-C	12		47							
MI 0471 (RPT)	12		48							
MT 0520-L	8									
MT 0520-L (RPT)	9									
BA 0300-M			90		< 1		< 0.5			
BA 0300-M (RPT)			90		< 1		< 0.5			
BA 0221-X			32							
BA 0221-X (RPT)			32							
MT 0281-C			12							
MT 0281-C (RPT)			12							
SU 0401-C			52							
SU 0401-C (RPT)			49							
RE 0541-C	1	6.9	10	2	< 1	< 1	< 0.5			
RE 0541-C (RPT)	1	6.2	8	2	< 1	< 1	< 0.5			
SU 0691-C	1		48	1	< 1	< 1	< 0.5			
SU 0691-C (RPT)	3		49	1	< 1	< 1	< 0.5			
SU 0921-C	< 1		290	< 1	< 1	< 1	< 0.5			
SU 0921-C (RPT)	< 1		280	< 1	< 1	< 1	< 0.5			
WE 0040-C				< 1	< 1		< 0.5	7.35	133	
WE 0040-C (RPT)				2	< 1		< 0.5	7.35	133	

domestic situations.

Two points about the testing procedure followed should be noted. The first is that the tests were carried out chronologically in the order given in the following tables; that is, high pH tests first followed by progressively more acidic solutions, and short duration tests before the longer static tests. The second is that the 10 day static tests for the first set of studies on pH variation were carried out on one set of pipes, and the remaining tests used the other set of pipes. In the 4°C, 30°C and soft water tests, the same pipes were used for the short duration tests and 10 day test. Both sets of pipes were prepared in exactly the same manner, but some anomalous behaviour can, to some extent, be attributed to the different total lengths of time that the two sets of pipe contacted the test solutions.

This anomalous behaviour was most noticeable in the very first experiments conducted on the three different pipes. These experiments at pH 8.0 using hard water at 20°C generally always gave high values compared to the next tests carried out. These tests were repeated at the end of the laboratory study and the results reported in the tables containing the temperature variation study (Tables 3.6 to 3.8). The experimental conditions are the same as the first set of entries in the first data tables (Tables 3.3 to 3.5), except that in the latter tables, the pipe was new, whereas in the former, the pipes had been in contact with a variety of test solutions.

3.2.1 Effect of pH

Copper pipe is the one found in the majority of the survey and

showed some clear trends in the laboratory study. The results of varying pH on the leaching of metals from copper pipe in hard water at 20°C are given in Table 3.3. In this table, as in all of the tables for the laboratory study, a value for the blank is provided. The results for the test solutions have not been corrected for this usually low number in order to show possible depletion of certain elements during the tests.

The copper test coils used in this study have 17 soldered joints, which is approximately half the average number of soldered connections in a normal house according to a commercial plumbing establishment. As such, the coils probably contain more soldered connections than would be found in house systems leading to one given outlet.

As can be seen in the Table, no Co or As was found at concentrations higher than the detection limit in any test solution. These elements were also never seen above the detection limit in any other tests with the other pipe materials.

The level of Cd was also consistently low even at low pH, in concurrence with the low values found for this element in the survey of Canadian drinking water (6).

The levels of Ni - high at 12 hours are erratic, but low (5.5 ± 5.7 ug/l). There is also no discernable correlation with the levels of other elements.

The lead levels rise to an apparent equilibrium in 2-12 hour contact time at higher pH values and show a much more rapid rise in more acidic conditions. The results at the highest pH, the first tests performed on this pipe, seemed anomalously

high. This is also observed when these values at 20°C are compared to the values obtained at a later date for the low and high temperature tests shown in Table 3.6. Therefore the tests at 20°C and pH 8 were repeated and these results are given in that table. These tests were also repeated for the other pipe materials (vide infra).

Using these results, instead of those in Table 3.6 for pH 8 only, reveal a definite trend. The Pb levels increase progressively with decreasing pH, increasing by approximately a factor of 5 in dropping the pH from 8 to 6, and increasing again by a further factor of 2 at pH 2. At pH 8, both the dynamic level of 63 ug/l and approximate equilibrium value for the static tests of 200 ug/l are higher than those of the survey or generally reported in the literature. Such elevated levels were found in the study of new pipes (12) in Britain, where electrolysis due to the presence of residues of the flux used in soldering was implicated. In the tests here, some of the effect may be ascribed to the relatively larger number of soldered joints in the test coil compared to those in the pipes leading to any one tap in a house. Another factor is the absence in these tests of a protective film of corrosion product that would occur in houses over a prolonged period. The four fold reduction in the level of lead comparing the static and dynamic tests, however, agrees well with values found in the literature (10).

Similar anomalously high values for Zn are observed in the first tests at pH 8 in Table 3.3 compared with the values in the Table 3.6. Also, the first two 10 day static tests are very high. This observation is not seen in the results for Pb and suggests the presence of Zn contamination on the surface of new copper pipe which is removed rapidly in the first 10 to 20

TABLE 3.3

Leaching of Metals from Domestic Water Supplies
(Hard Water) on Copper Pipe at 20°C

pH	Flowing Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
8	Blank	< 0.5	< 1	6	3	1	1.4	< 1
	D ⁺	< 0.5	< 1	140	7	1	38	< 1
	S [±] , 2h	< 0.5	< 1	550	1,800	2	270	< 1
	S, 12h	< 0.5	< 1	400	1,200	9	170	< 1
	S, 10d	< 0.5	< 1	380	2,400	< 1	467	< 1
6	Blank	< 0.5	< 1	10	30	1	1.4	< 1
	D	< 0.5	< 1	200	85	1	22	< 1
	S, 2h	< 0.5	< 1	4,600	965	20	860	< 1
	S, 12h	< 0.5	< 1	3,200	1,232	13	1,265	< 1
	S, 10d	1.4	< 1	1,750	1,475	8	6,300	< 1
	Blank	< 0.5	< 1	9	16	2	1.1	< 1
	D	< 0.5	< 1	1,320	1,000	1	170	< 1
	S, 2h	< 0.5	< 1	9,000	1,914	2	620	< 1
	S, 12h	< 0.5	< 1	8,200	1,914	9	1,133	< 1
	S, 10d	1.2	< 1	2,350	2,200	4	560	< 1
2	Blank	< 0.5	< 1	13	10	< 1	2.7	< 1
	D	< 0.5	< 1	80,000	723	7	1,166	< 1
	S, 2h	< 0.5	< 1	145,000	1,132	1	1,965	< 1
	S, 12h	< 0.5	< 1	210,000	1,265	14	2,031	< 1
	S, 10d	< 0.5	< 1	9,000	2,400	8	920	< 1

⁺ D denotes as dynamic condition; [±] S denotes static condition

days of service. The Zn levels increase by a factor of 10 to 100 in decreasing the pH from 8 to 2 and, as for Pb, show a more rapid approach to equilibrium and lower pH's. The Zn values for the dynamic test agrees well with survey results and the static tests at pH are lower, but not dramatically, than the survey results.

The results for copper are not so clear. Using only the results for up to 12 hr contact time in Tables 3.3 and 3.6, the level of copper approaches an equilibrium of ca 1 mg/l at pH 8 and progressively higher levels at lower pH's, increasing by a factor of 2 to 4 at pH 6. There is an apparent dramatic increase at pH 2. The value at pH 8 is higher than found in the survey, which may be ascribed to the lack of a film of carbonate scale or corrosion product on the pipe which should slow the rate of copper release. The results do suggest however, that a drop of pH to 6 should significantly increase the solvency of Cu in copper pipes and would result in an increase in the number of houses that would exceed the recommended limit for Cu in the first-draw waters.

The 10 day static test results are anomalously low, and the reason for this is not clear. This may be due to redeposition of Cu after 12 hour contact time but no reasonable explanation seems to be available. It appears more likely that there are differences between the two test pipes, although they were prepared in as similar a fashion as possible.

Galvanized pipe showed some quite large aging effects for pipes in contact with water up to 20 days. The results for the test of varying pH are given in Table 3.4 and, as above, different repeat test results for pH 8 at 20°C in Table 3.7. As with the copper pipe, no Co or As was observed, and the Ni results were quite low and showed no correlation with pH or contact time.

TABLE 3.4

Leaching of Metals from Domestic Water Supplies
(Hard Water) on Galvanized Pipe at 20°C

pH	Flowing Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
8	Blank	< 0.5	< 1	6	3	1	1.4	< 1
	D ⁺	< 0.5	< 1	12	17	< 1	1,800	< 1
	S [‡] , 2h	< 0.5	< 1	6	18	1	12,800	< 1
	S, 12h	< 0.5	< 1	90	93	19	19,600	< 1
	S, 10d	< 0.5	< 1	2	200	< 1	80,000	< 1
6	Blank	< 0.5	< 1	10	30	1	1.2	< 1
	D	< 0.5	< 1	54	80	< 1	1,920	< 1
	S, 2h	< 0.5	< 1	24	53	6	1,940	< 1
	S, 12h	< 0.5	< 1	29	90	1	28,700	< 1
	S, 10d	< 0.5	< 1	1	170	2	66,000	< 1
	Blank	< 0.5	< 1	9	16	2	1.1	< 1
	D	1.7	< 1	18	18	1	6,800	< 1
	S, 2h	< 0.5	< 1	10	25	2	16,000	< 1
	S, 12h	< 0.5	< 1	12	70	7	35,300	< 1
	S, 10d	< 0.5	< 1	10	47	2	18,400	< 1
2	Blank	< 0.5	< 1	13	10	< 1	2.4	< 1
	D	0.9	< 1	165	390	7	268,000	< 1
	S, 2h	1.0	< 1	37	310	9	308,000	< 1
	S, 12h	1.8	< 1	18	230	1	329,000	< 1
	S, 10d	< 0.5	< 1	8	33	< 1	62,000	< 1

⁺D denotes dynamic condition; [‡]S denotes static condition

Lead and Zn values apparently rise and fall together indicating a common source and release pattern in the pipes. The lead is a contaminant of the Zn coating applied during galvanization (16) and the observed correlation of these two elements is consistent with this. Looking only at the tests up to 12 hours for Zn indicates that no equilibrium value has been reached. Also, the very first tests at pH 8 are higher than expected from the rest of the tests, and the results at 20°C in Table 3.7 confirm this anomalous behaviour. A trend to progressively higher rates of leaching of Zn can be seen as the pH is lowered, the levels increasing by approximately a factor of 2 at pH 6, and very large increases at pH 2. The results of the 10 day tests at pH's 4 and 2 confirm this trend, but the absolute values are significantly lower. There appears to be a very high rate of Zn release for new pipe which drops substantially during the first 10-20 days of use. Even after 20 days however, the rate of Zn release continues to decrease with time (see Sec. 3.2.2). The observed Zn levels are generally substantially higher than observed in the survey samples; an indication of the importance of the buildup of a corrosion product film in the galvanized pipe in houses (1). Similar results are seen for the Pb values, which are substantially higher in the laboratory tests compared to the survey results.

The observed levels of copper are quite low even for the first tests, and become generally lower as the length of time the pipe is used increases. The copper levels do not correlate well with Zn values, suggesting that copper is not a contaminant in the zinc coating. However, the 10 day static tests all show levels at, or below, the blank level, which indicates that redeposition of the metal may be occurring upon protracted stagnation of water in galvanized pipe.

TABLE 3.5

Leaching of Metals from Domestic Water Supplies
(Hard Water) on Lead Pipe at 20°C

pH	Flowing Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
8	Blank	0.7	< 1	4	2	< 1	2.2	< 1
	D ⁺	1.1	< 1	14	100	< 1	3.5	< 1
	S [#] , 2h	1.0	< 1	10	300	< 1	1.3	< 1
	S, 12h	1.3	< 1	26	600	< 1	2.0	< 1
	S, 10d	< 0.5	< 1	27	475	< 1	2.3	< 1
6	Blank	< 0.5	< 1	12	2	2	3.3	< 1
	D	< 0.5	< 1	16	1,375	< 1	6.5	< 1
	S, 2h	< 0.5	< 1	9	18,600	< 1	23	< 1
	S, 12h	< 0.5	< 1	7	34,000	< 1	8.5	< 1
	S, 10d	1.2	< 1	12	2,600	2	98	< 1
	Blank	< 0.5	< 1	8	2	3	2.2	< 1
	D	< 0.5	< 1	10	18,000	3	4.7	< 1
	S, 2h	< 0.5	< 1	13	50,000	4	2.5	< 1
	S, 12h	< 0.5	< 1	8	75,000	4	1.9	< 1
	S, 10d	< 0.5	< 1	7	14,600	2	99	< 1
2	Blank	< 0.5	< 1	4	3	2	2.9	< 1
	D	< 0.5	< 1	8	6,200	3	3.2	< 1
	S, 2h	< 0.5	< 1	9	7,200	4	2.9	< 1
	S, 12h	< 0.5	< 1	7	7,400	5	2.6	< 1
	S, 10d	1.4	< 1	13	21,300	3	121	< 1

⁺ D denotes dynamic condition; [#] S denotes static condition

The lead pipe showed quite different behaviour in the two pipes used, probably due to a build-up of insoluble lead compounds on the surface which reduces the rate of lead release. The results for these tests are given in Table 3.5, with repeat tests for pH 8 given in Table 3.8. The difference in behaviour of the two pipes can be seen in the results for Cd, where the pipe used for the dynamic and short term tests showed measurable concentrations for the first test, while the pipe used for the 10 day static tests only showed Cd at lower pH values.

The Pb values for the 10 day tests show an increase in concentration with decreasing pH, increasing 5 fold at pH 6 and a further 10 fold by pH 2, a result expected and found in other studies (9, 11). The results for the shorter term tests however, show a peak level at pH 4 which is substantially higher than the 10 day tests. These results indicate that the pipe used for these shorter tests had a substantially cleaner surface than the other pipe, and that a buildup of a protective film required a significant time to form. This same pipe was used in the tests at 4 and 30°C in Table 3.8, the soft water tests in Table 3.9 and the repeat tests at pH 8 and 20°C in Table 3.8. The results in this table indicate that the rate of release of Pb was continuing to decrease slightly even at this point. The effect of pH on lead pipe thus only appears in the 10 day tests. The results in Table 3.8 for different times of contact, which were all carried out on the same pipe, indicate that the lead levels do not reach an equilibrium value at 12 hours, and increased leaching of the metal continues for up to 10 days.

The values for Ni in these tests are all at, or near, the detection limit and indicate no significant releases of this

element. Zn appears only in the 10 day tests at pH 6 and lower. The low values for the other pipe even at the beginning of the tests suggest either a mechanism of trapping Zn in the protective film as it is forming, or a chemical difference between the two pipes.

The copper concentrations are all low and show no apparent correlation with pH. The levels are at or below the blank value and might indicate absorption of this element onto the walls of the pipe.

3.2.2 Effect of Temperature

Tests were also carried out at 4 and 30°C to test the effect of temperature on the leaching of metals from pipes. These tests, carried out at pH 8 using hard water, showed that the first tests carried out at 20°C, pH 8 were anomalous and so these latter tests were repeated. The results obtained for these repeated tests, and the results at other temperatures, are given in Tables 3.6, 3.7 and 3.8 for copper, galvanized steel and lead pipe respectively.

The results for copper pipe in Table 3.6 show little or no effect on either the equilibrium concentration of copper, (ca 1 mg/l) or the time required to reach equilibrium, which is 2-12 hours. The values for Pb and Zn show a slight rise at higher temperatures, but this may be a kinetic phenomenon of the higher temperature increasing the rate of approach to same equilibrium value.

The results for galvanized pipe, in Table 3.7, may suffer from aging effect problems described in 3.2.1. Thus the levels of Zn and Pb are anomalously low at 20°C compared to the results

at 4 and 30°C which were obtained earlier. The results at 4 and 30°C, however, do indicate a significant temperature effect on both of these elements which increase in concentration by up to 4 times for the 10 day tests. Cu and Ni, however, show no significant temperature effect and the levels stay close to the concentration in the blank.

The effect of a buildup of a protective coating on the lead pipe is seen quite clearly in the results for Pb release in Table 3.8. The results for the temperatures 4 and 30°C indicate an increase in release of Pb and Zn as the temperature rises. The approximately 2 fold increase in the concentration of Pb is probably an under-estimate since, as mentioned in 3.2.1, this pipe showed a constantly decreasing rate of release of Pb after the middle of the tests varying pH. Since the 20°C test was carried out after the 30°C test, the relative change in lead concentration may be somewhat higher. Neither Cu or Ni show any increase in concentration with increasing temperature.

Overall, increasing temperatures would appear to be of concern only for Pb, the concentration of which increases with temperature in all three pipes. The effect is most marked for lead pipe where both dynamic and static levels are affected. For copper pipes, the overall effect is much less, and is seen only for static tests.

3.2.3 Effect of Hardness

Tests were carried out on the pipes using synthetic soft water (22.4 mg/l as CaCO_3) at pH 8 and 20°C. The results are given in Table 3.9, and should be compared to the results for 20°C given in Tables 3.6 - 3.8 since the pipes were of

TABLE 3.6

Effect of Temperature on Copper Pipe at pH 8, Hard Water

Temperature	Flow Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
4°C	Blank	< .5	< 1	8	1	1	1.4	< 1
	D	< .5	< 1	140	44	1	22	< 1
	S, 2h	0.5	< 1	660	81	2	19	< 1
	S, 12h	< .5	< 1	1,450	137	5	14	< 1
	S, 10d	< .5	< 1	1,000	225	3	25	< 1
20°C	Blank	< .5	< 1	3	< 1	1	1.2	< 1
	D	< .5	< 1	232	63	1	5.5	< 1
	S, 2h	< .5	< 1	756	138	2	9.8	< 1
	S, 12h	< .5	< 1	1,152	169	9	15.6	< 1
	S, 10d	< .5	< 1	1,000	210	2	22.0	< 1
30°C	Blank	< .5	< 1	5	1	< 1	1.3	< 1
	D	< .5	< 1	260	59	< 1	6.5	< 1
	S, 2h	< .5	< 1	750	176	< 1	12.5	< 1
	S, 12h	< .5	< 1	1,250	300	< 1	13.5	< 1
	S, 10d	< .5	< 1	751	300	3	50	< 1

TABLE 3.7

Effect of Temperature on Galvanized Pipe at pH 8, Hard Water

Temperature	Flow Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
4°C	Blank	< .5	< 1	10	1	1	1.2	< 1
	D	< .5	< 1	8	8	3	3,100	< 1
	S, 2h	< .5	< 1	7	7	3	7,100	< 1
	S, 12h	< .5	< 1	5	21	< 1	15,200	< 1
	S, 10d	< .5	< 1	5	12	< 1	8,200	< 1
20°C	Blank	< .5	< 1	3	< 1	1	1.2	< 1
	D	< .5	< 1	3	3	< 1	1,609	< 1
	S, 2h	< .5	< 1	6	3	1	1,560	< 1
	S, 12h	< .5	< 1	< 1	23	1	1,755	< 1
	S, 10d	< .5	< 1	4	4	2	6,000	< 1
30°C	Blank	< .5	< 1	4	1	< 1	1.3	< 1
	D	< .5	< 1	7	14	< 1	6,900	< 1
	S, 2h	< .5	< 1	6	12	2	5,900	< 1
	S, 12h	< .5	< 1	6	10	< 1	5,800	< 1
	S, 10d	< .5	< 1	15	70	8	29,000	< 1

TABLE 3.8

Effect of Temperature on Lead Pipe at pH 8, Hard Water

Temperature	Flow Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
4°C	Blank	< .5	< 1	11	1	1	1.4	< 1
	D	< .5	< 1	18	650	< 1	1.5	< 1
	S, 2h	< .5	< 1	9	1,500	< 1	2.2	< 1
	S, 12h	< .5	< 1	7	2,150	< 1	1.9	< 1
	S, 10d	< .5	< 1	1	3,800	2	2.6	< 1
20°C	Blank	< .5	< 1	3	1	< 1	1.2	< 1
	D	< .5	< 1	13	250	< 1	2.0	< 1
	S, 2h	< .5	< 1	7	531	< 1	1.6	< 1
	S, 12h	< .5	< 1	9	1,031	< 1	1.6	< 1
	S, 10d	< .5	< 1	6	950	< 1	1.3	< 1
	Blank	< .5	< 1	5	1	< 1	1.3	< 1
	D	< .5	< 1	10	1,025	< 1	2.6	< 1
	S, 2h	< .5	< 1	8	2,400	< 1	14.5	< 1
	S, 12h	< .5	< 1	< 1	3,500	< 1	1.6	< 1
	S, 10d	< .5	< 1	5	6,400	1	5.0	< 1

comparable age at that point. The data indicate remarkably little effect on the leaching of any elements except for Zn and Cu leached from the copper pipe. These two metals are surprisingly less soluble in soft water, compared to hard, at this pH.

Soft water is usually associated with more aggressive attack of piping materials (1-5) and the lack of an effect in this test is unexpected. It should be noted however, that aggressiveness in water in distribution systems is a function both of pH and hardness. It is apparent that both of these parameters need to be lowered to produce significant changes in the rate of leaching of metals. Dramatic increases in the rate of release of Pb from lead pipe have been observed only at low pH (7) and at very low hardness levels (15 mg/l as CaCO_3) (10).

Another factor involved is also likely the length of time the pipe is in service. Thus only small increases in the corrosive properties of water in pipes may lead to substantially increased leaching rates, but only over a long period of time. Slight pitting and scaling will dramatically increase the surface area available for desorption of metals and thus greatly increased rates of contamination.

3.3 SURVEY STUDY

A total of 105 sites in Metropolitan Toronto and surrounding areas were sampled, yielding a total of 210 water samples. The analytical data for all analyses are given in Appendix C. The samples were assigned identification codes of the following format:

XXDDDD-Y

where XX is a general location indicator. The values and meanings are given in Table 3.10. DDDD is a 4 digit number in

TABLE 3.9

Leaching of Metals from Domestic Water Supplies
(Soft Water) at pH 8 and 25°C

Piping Material	Flow Condition	Cd	Co	Cu	Pb	Ni	Zn	As
ppb								
Galvanized Pipe	Blank	< 0.5	< 1	< 1	< 1	3	0.5	< 1
	D	< 0.5	< 1	2	9	2	970	< 1
	S, 2h	< 0.5	< 1	6	2	4	1,930	< 1
	S, 12h	< 0.5	< 1	< 1	1	< 1	1,430	< 1
	S, 10d	< 0.5	< 1	1	< 1	1	1,830	< 1
Copper Pipe	Blank	< 0.5	< 1	< 1	< 1	3	0.5	< 1
	D	< 0.5	< 1	123	85	2	1.1	< 1
	S, 2h	< 0.5	< 1	204	127	< 1	1.3	< 1
	S, 12h	< 0.5	< 1	230	146	< 1	2.3	< 1
	S, 10d	< 0.5	< 1	92	111	< 1	5.7	< 1
Lead Pipe	Blank	< 0.5	< 1	< 1	< 1	3	0.5	< 1
	D	< 0.5	< 1	2	700	1	10	< 1
	S, 2h	< 0.5	< 1	5	500	< 1	7.7	< 1
	S, 12h	< 0.5	< 1	3	1,000	< 1	5.5	< 1
	S, 10d	< 0.5	< 1	< 1	5,200	1	12	< 1

which each sampling site was numbered sequentially by powers of 10. The standing samples at each site are assigned numbers that are a multiple of 10, and the running samples are 1 greater. The character Y is a code for the principal material used in the plumbing system for each site, as determined from the questionnaire. The values and meanings for this code are also given in Table 3.10.

The boundaries for the general location indicator in the identification code are also marked. The sample sites can be correlated with the analysis data in Appendix C by the sample number. The four digit number in the identification code is equal to the sample number times ten for the standing sample, and the sample number times 10 plus one for the running samples. For example, sample identification code MT0630-C is the standing sample for site 63. The site is in metropolitan Toronto and the major plumbing material is copper pipe. Identification code MT0631-C is the running water sample from the same site.

The samples are listed in the order in which they were collected, and for each site, the order is static sample first, then dynamic sample. The majority of the sites (64%) were private residences built since 1944 having copper plumbing. Seven institutional sites were sampled. One new house that was not yet occupied and eight houses built before 1930 were sampled.

As can be seen in the listing, neither As nor Co was detected at any of the sites. The pH showed very little variation over

TABLE 3.10

Location Codes for Survey Study

MT	Toronto (Metropolitan)
SC	Scarborough
MI	Mississauga
BR	Brampton
BA	Bramalea
DW	Downsview
ET	Etobicoke
SU	Suburbs
RE	Rexdale
WE	Weston

Plumbing Material Codes for Survey Study

C	Copper
G	Galvanized Steel
L	Lead
M	Mixed
X	Unknown

the entire survey, and the hardness was significantly different at only 6 sites. Three sites used water softeners and three sites at locations north of Toronto had higher hardness values. Thus no significant correlations with these parameters can be expected.

Arithmetic and log transformed statistics and correlation coefficients for the survey as a whole are given in Appendix D. The bimodal nature of the population is clear for those elements that showed consistently measurable levels: Cu, Pb and Zn. Values of the geometric mean and median extracted from appendix F are given in Table 3.11.

As a first cut of the population, the survey results were divided into two subpopulations consisting of all standing samples in one and all running samples in the other. The statistics listings for these populations are given in Appendix E, and the geometric mean and median values are tabulated in Table 3.11.

The best correlations for Cu in the standing water samples is with Pb and Cu in the running samples. The latter is expected, and the former could have been anticipated from the results of the laboratory study of the release of Pb from copper pipes. The decrease in average concentration of Cu after flushing of the pipes (9 fold for the arithmetic mean and 13 fold for the geometric mean) agrees well with the value of 5-10 fold observed in the laboratory study of copper pipes at pH 8.

The log transformed histograms for lead indicate that neither population is very log-normal. The laboratory studies indicate that lead is leached from all three pipe materials at significant, but different, rates. Thus the underlying

inhomogeneity of the population shows up more clearly here than for copper, for which significant leaching occurs only in copper plumbed houses. The enrichment of lead in the standing samples compared to the running ones (7 fold for arithmetic mean, 4 fold for the geometric mean) agrees well with the factors observed in the laboratory study. Lead concentrations greater than 0.05 mg/l were observed only in the standing samples and in only 6 sites. The highest level seen (1.06 mg/l) was for site MI0660-C, which was the new house that had not yet been occupied. The high value is probably caused by the long contact time, and the likely presence of soldering fluxes in the pipes, which results in greater releases of Pb (12).

The mean levels for Ni are low, as found for all test pipes in the laboratory study. It is also clear from the histograms in Appendix E that the true population means are below 1 ug/l.

No samples contained Zn concentrations greater than the recommended value. The enrichment factors for the standing samples compared to the running samples (6 fold for arithmetic mean, 13 fold for logarithmic mean) bracket the 10 fold increase that can be estimated from the laboratory study of galvanized pipe at pH 8.

Cd was never found to exceed the recommended level and was observed at a measurable level in only 7 samples. Five of these samples were collected at 3 institutions: MT1150-X, the Mining Building, and MT1140-X, the Institute of Environmental Studies at the University of Toronto, and MT1190-C, the Royal Ontario Museum. All three sites also showed rather high levels of Zn in both the standing and running samples which indicate the presence of a substantial length of galvanized pipe in the

plumbing system leading to the tap sampled. One of the other sites showing a measurable Cd level, MT1130-G, is a house built in 1880 which has galvanized pipe in the plumbing.

A list of the more unusual sites samples is given in Table 3.12 to aid in assessment of the survey results.

3.4 U.S. SURVEY

The preliminary statistics on 500 samples from Dr. Strain are given in Appendix F. These statistics are based on the entire sample set as one population and indicate the range, and distribution, of the measured parameters. Hardness was not measured in this survey, and the values shown in the tables are calculated from the concentrations of the major polyvalent cations, principally Ca and Mg. Values of the geometric mean and median are given in Table 3.13. These results show that the average pH level is similar to the results of the Toronto survey but that the average hardness is substantially lower in the U.S. results. The Cu levels are similar, but all other elements are found at higher levels in the U.S. survey. In the U.S. survey, only one standing sample was collected at each site, and so comparisons should only be made with the corresponding results for the Toronto survey.

A subpopulation of the U.S. results was selected by taking samples of pH in the range 7.1 to 7.9 and hardness 100 to 200 mg/l as CaCO_3 . There were 54 samples in this set and the statistics are given in Appendix G. The geometric mean and median values are also given in Table 3.13. It can be seen that the levels of the elements analyzed in this work are not substantially different in the subpopulation compared to the 500 samples for the whole population. It should be noted that

TABLE 3.12

Description of some specific sampling sites.

Houses built before 1900.

MT 1100-X	(1875)
MT 1150-X	(1877)
MT 1120-M	(1880)
MT 1130-G	(1880)

Houses built 1900-1920.

MT 1140-X	(1904)
MT 0990-X	(1910)
MT 1190-X	(1912)
MT 0940-C	(1915)
MT 0950-M	(1920)

Houses built 1921-1940.

MT 1200-G	(1922)
MT 0520-L	(1930)
MT 1060-X	(1931)

New house before occupation.

MI 0660-C

For location and plumbing codes, see Table 3.10.

the observed levels of metals in this survey are due to the concentration in the supply water at each site plus elements leached from the distribution system in each house, and that the relative contribution of each is impossible to estimate.

TABLE 3.13

Geometric Mean and Median Values of Selected Parameters
in the U.S. Survey

Population		Parameter						
		pH	Hardness mg/l CaCO ₃	As ppb	Cd ppb	Cu ppb	Pb ppb	Zn ppb
1. Whole ^{a)}	G.M.	7.70	69	40	2	60	30	168
	Median	7.85	88	< 20	< 1	100	< 20	266
2. Hardwater ^{b)}	G.M.	7.60	141	30	1	70	20	253
	Median	7.70	144	< 20	< 1	140	< 20	351

a) Based on 500 samples of standing water.

b) Subpopulation of 54 samples with pH in range 7.1 to 7.9 and hardness in range 100 to 200 mg/l as CaCO₃.

4. SUMMARY

Laboratory studies of the effect of pH, temperature and hardness on the leaching of metals from domestic plumbing materials are completed. The results indicate that significant changes occur in new pipe material during the first few weeks of contact with water. However, the effect of decreasing pH can be discerned and results in increased rates of leaching of metals, principally lead, copper and zinc, from piping materials. A decrease of pH from 8 to 6 can result in substantial increases in the leaching of lead and copper from the most widely used plumbing material, soldered copper pipes.

The effect of temperature is slight, up to 30°C, for all metals, except lead and it is difficult to separate the effects on both rate of leaching and equilibrium values. No significant effect of soft water was observed. It seems likely that the corrosive action of soft water, possibly softer than that used in this study, at lower pH values than 8 will produce observable effects.

The survey of 105 sites in the Toronto area completed in this study show some good correlations with the results of the laboratory study, particularly the effect of a lowering of metal concentrations after flushing the water system compared to levels in standing water. Only lead was found at concentrations higher than the recommended level, at some sites, and then, only in the standing samples. The pH values in all of the samples are essentially the same, as are the hardness levels, and this precludes any statistical analysis of these parameters. The effects of pH, and hardness, on field samples must thus await further survey work.

The survey does highlight some other useful points. The collection of both a static and dynamic sample at each test site, is useful in observing the more dramatic effects of leaching of metals from different pipe types in the static tests. It also usefully investigates the effect of flushing on the metals concentration, and in the survey done here, indicates that for larger buildings, even a 5 minute flush does not effectively reduce the concentrations of some metals. For house plumbing systems, it also delimits the range of metals' concentration that are delivered at the tap.

the aging effect observed in the laboratory study, that new plumbing pipes release substantially higher levels of metals than older pipes. Field sampling of new houses up to several months old would be necessary to clarify the magnitude of the increase, and also its duration.

The results of the laboratory study on the effect of lowered pH indicate that higher levels of metals, particularly lead, in drinking water can be expected with every decrease in pH. Houses that use municipal water supplies seem unlikely to be affected since buffering and pH adjustments by the water treatment facility to conform to government acceptable levels will be carried out. However, houses and cottages that rely on river and well water may be affected, particularly when situated in the soft water areas that are particularly susceptible to the effects of acid rain. A survey of such sites in areas of known susceptibility should be carried out to determine the levels of metals in tap water. Even in areas where heavy metal contamination of water supplies is low, it is clear from this study that substantial contamination due to leaching from the plumbing pipes may be occurring.

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APPENDIX "A"

Subject: B.M.L. Survey Study

Ref: #'s _____/_____

Sampling Date: _____

Delivery Date: _____
(to C. Vairo B.M.L.)

Dear

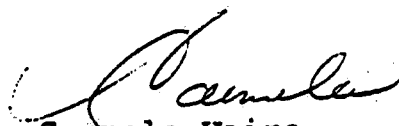
B.M.L. is conducting a Survey Study of domestic tap water among all B.M.L. and B.R.L. staff. Your co-operation in assisting B.M.L. with the survey is essential to the success of the study. Each B.M.L./B.R.L. employee will be requested at some time over the next 2-3 months to carefully follow the attached sampling instructions and conscientiously complete the enclosed Questionnaire: Section A to C.

The exact date of your individual participation is indicated in the top right hand corner of this letter. In addition, you will find an identification reference number which should correlate to the questionnaire and the collected samples. If the above date is inconvenient, please contact me as soon as possible to arrange an alternative date.

If there are any questions regarding the survey study as outlined, please feel free to enquire.

Yours sincerely

BARRINGER MAGENTA LIMITED



Carmela Vairo
Research & Marketing Administrator

CV/pa

NB. This study is to be kept in Strict Confidence.

B.M.L. Survey Study

Introduction

The role of each household in this survey is to supply two samples of water from their kitchen cold water taps. One is to be drawn first thing in the morning before any other water in the house has been run; this will constitute the "first draw" sample. The second sample, herein known as the "second draw", is to be taken after the water has been left running for 5 minutes. Each participant household will be supplied with two 600 ml screw-top plastic bottles for sample collection.

The scheduled plan is such that Barringer personnel, in preselected groups of approximately 25, will be requested to follow the attached sampling instructions and to return the samples on the same morning of the sampling day.

Sampling Instructions

IMPORTANT: GENERAL INSTRUCTIONS

1. To prevent contamination and to ensure validity of data, please do not remove the top of the plastic bottle prior to sample collection; in addition, please do not touch the neck or tip of bottle with your fingers during sample collection.
2. Collect samples exactly as per instructions..
3. Please bring the samples collected to work that same day and drop them off at Carmela Vairo's office first thing in the morning. Any problems incurred in sample collection should be communicated at that time as well as explained in Section C.

"FIRST DRAW" SAMPLE

1. Initially review the General Instructions if you have not already done so.
2. The "first draw" sample is to be collected from your kitchen cold water tap on the morning of the date specified by the covering letter.
3. It is imperative to the success of the study that the "first draw" sample be collected before any other water in the household has been run that particular morning.
4. Simply fill the plastic bottle labelled "first draw" sample completely full and then, replace the screw-top securely.
5. Store the sample prior to coming to work that morning in a safe place at room temperature.
6. Complete the questionnaire portion of Section C.
7. Follow the attached sampling instructions for the "Second Draw" sample.

"SECOND DRAW" SAMPLE

1. The second draw sample is to be collected from your kitchen cold water tap on the morning of the date specified by the covering letter.
2. It is imperative to the success of the study that the "second draw" sample be collected from your kitchen cold water tap the morning of the date specified only after the kitchen's cold water tap has been left running for 5 minutes.
3. Simply fill the plastic bottle labelled "second draw" sample completely full then, replace the screw-top securely.
4. Store the sample prior to coming to work that morning in a safe place at room temperature.
5. Complete Section C of the questionnaire and refer to part 3 of the General Instructions.

SURVEY STUDY QUESTIONNAIRE

Section A

B.M.L. Use Only

1. Name & Address _____

2. Reference Number _____

3. Date of Sampling _____

4. Is this dwelling?:

(Please check the appropriate box)

a private residence (single home,

(duplex, townhouse) ☐

an apartment/condominium bldg. ☐

5. Do you know how old this building is?:

was it built before 1919 ☐

was it built between 1919 & 1944 ☐

was it built after 1944 ☐

6. In your best estimation, state the
approximate year this building was
built?: _____

7. How many persons are normally resident,
for at lease six months in the year,
in this household?: _____

Section B

3.M.L. use only

8. Does the supply water pipe go directly to a storage tank before going to the kitchen cold water tap?

(Please check the appropriate box)

Yes ☐

No ☐

If your answer was "Yes" go on to answer # 9 & 10.

If your answer was "No" go on to answer # 11.

9. What is the estimated length of pipe & type of pipe material (e.g. copper, lead or galvanized; or a combination), between the pipe entering the dwelling & reaching the storage tank?

<u>Length of Pipe (ft.)</u>	<u>Material</u>
_____	_____
_____	_____
_____	_____

10. What is the estimated length of pipe and type of material (e.g. copper, lead, galvanized; or a combination), between the pipe leaving the storage tank and reaching the kitchen tap?

<u>Length of Pipe (ft.)</u>	<u>Material</u>
_____	_____
_____	_____
_____	_____

Section B (cont'd)

B.M.L. use only

11. What is the estimated length of pipe and type of pipe material, (e.g. copper, lead or galvanized; or a combination) between the pipe entering the dwelling and reaching the kitchen tap?

<u>Length of Pipe (ft.)</u>	<u>Material</u>
_____	_____
_____	_____
_____	_____

SECTION C

B.M.L. use only

12. "First Draw" Sample: In your estimation what was the time lapse (hrs.) between the sample collection in the morning and the previous evening's cease of use of the water system?

13. "Second Draw" Sample: In your estimation what was the lapse of time (min.) that the water from the kitchen cold water tap was left to run before the "second draw" sample was taken?

14. If you incurred any problems in sample collection, please elaborate in the space below:

OPERATION OF THE HYDRIDE GENERATION SYSTEM

There are four separate units:

- a) Sample manifold, pump, gas separator, furnace
- b) Technicon auto sampler
- c) Honeywell recorder
- d) Variac

1. Set up such that the liquid-gas separator is directly in front of the furnace, vertical and there is not very much strain on the furnace. Connect the gas separator to the furnace with the side arm of the furnace about $\frac{1}{4}$ cm into the tygon tube.
2. Lock the pressure plates of the pump into position for all channels. (At some point make sure to check the condition of the tubing as the plastic composition of the pressure plates is attacked by acid). Replace digestive tubing as necessary.
3. Make the following interconnections and settings:
 - a) A.A. to Furnace

Turn A.A. on with the appropriate lamp in place. After warm-up of 15 minutes, optimize lamp position and select wavelength. Install the furnace. Align it with the beam by rotating, raising and moving front and back until a minimum is seen on the absorbance scale. Set the scale to zero.
 - b) A.A. to Recorder

Take the output cord from the back of the A.A. the red output clip goes to the red terminal on the recorder. The A.A. scale expansion set to minimum, damping at (D) maximum. Damper must be checked to ensure it is closed. (This is necessary to ensure

APPENDIX "B"

GFAAS STANDARD ANALYTICAL METHODS FOR
Cu, Pb, Zn, Ni, Co & Cd; Hydride AA for As,
and Hardness Determination.

a minimum of draft which disturbs the base-line. However, the room ventilation fan must be on). Recorder scale is usually 2 mv except for some high Se stds which might require the next lower expansion 5 mv scale.

c) Furnace to Variac

Always make sure Variac is on off position before touching the output leads. Clip them on to the ends of the nichrome heater sticking out of the sides of the furnace. These leads are interchangeable. Make sure that the exposed connections are not touching any other metal, neither should they be blocking the beam. Turn the variac on and make sure it glows bright red.

(It takes about 15 minutes to reach preset temp.)

d) Manifold to Auto Sampler

Insert the sample probe into the appropriate clip on the Auto Sampler. The light had been adjusted so that the prob touches the bottom of the tube when in the sampling position, otherwise the tube will snap when moving from rinse to sample. The replacement tube could be any appropriate length provided the end that goes into the tygon tube is fire-polished.

The instrumental parameters are as follows:

	As	Se	Tin
(1) Wavelength	193.7 nm	196.0 nm	286.3 nm
(2) Lamp current	7 mA	4.5 mA	60% of ma
(3) Slit width	300 u	300 u	100 u
(4) Instrumental damping	D	D	D
(5) Gas flow rate	0.5 scfh	0.5 scfh	0.5 scfh
(6) Acid conc.	2 N Hcl	6 N hcl	170
(7) Na BH4 conc.	170	170	170
(8) Recorder span.	2 mv full scale	2 mv full scale	2 mv full sc
(9) Recorder speed	5 Mins.	5 Mins.	5 Mins.
(10) Variac	21 V	20 V	22V
(11) Sample time	1 Min.	1 Min.	1 Min.
(12) Wash time	2 Min.	2 Min.	2 Min.
(13) Gilson pump	325	325	325

Sample Preparation:

(a) Water Sample:

As
2.5 ml sample + 1 ml
Conc. Hcl + 1.5 ml H₂O
D.F. x 2

Se
2.5 ml sample + 2.5 conc. Hcl
D.F. x 2

(b) Sediments and Soils:

250 mg sample + 0.5 - 1 ml conc. HNO₃
+ 2 ml HClO₄ - heat to fumes of HClO₄
Cool and make up volume to 5 ml with H₂O D.F. x 20

Turn On:

1. Turn on A.A. (3 switches) + lamp + acid adjust the slit width.
2. After warming up for about 15 minutes, optimize the conditions as in normal A.A. operation.
3. Turn variac that runs the furnace on. After about 15 minutes when it glows bright red, align the furnace by rotating, raising and moving back and front until a minimum is seen on the absorbance scale, then with the fine gain bring the scale to zero.
4. Apply all the pressure plates of the gilson pump.
5. Turn on the Argon tank and check the gas regulator for the particular gas flow rate.
6. Insert the 3 probes in corresponding solutions and turn the gilson pump on.
7. You may speed the rate of the flowing solutions by applying the rabbit jack switch until the gas separator is filled.
8. Release that switch and watch the system for a few minutes to make sure everything is going alright and there is no leak in the systems.
9. Turn the recorder on - wait for the base-line to settle then turn the auto sampler power on.

Turn Off:

1. Wait until sampler finishes last sample.
2. Shut off sampler power.
3. Let the gilson pump run one more minute in acid.
4. Turn as is recorder off.
5. Remove all 3 probes from bottles and transfer to water.
6. Let pump run in H₂O for a while (5 mins.) to replace the liquids in side tubing.
7. Meanwhile, after 1 minute of H₂O turn Argon off on tank. Also switch off variac that runs the furnace.
8. Shut pump off (to centre position).
9. Replace caps on reagent bottles.
10. Keep Na BH₄ in fridge.
11. Release all the pressure plates on gilson pump.
12. Shut off A.A. (3 switches) + lamp + power.

Interferences:	As	Se	Ni	Cu
	Se	As	Cu	Ni

Detection limit: 1.0 ppb As and Se

Dilution: Should be done in the same acid matrix.

CADMIUM

Method 213.2 (Atomic Absorption, furnace technique)

STORET NO. 01027

Dissolved 01025

Suspended 01026

Optimum Concentration Range: 0.5–10 $\mu\text{g/l}$

Detection Limit: 0.1 $\mu\text{g/l}$

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.
3. Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3 .

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3 .

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Contamination from the work area is critical in cadmium analysis. Use of pipet tips which are free of cadmium is of particular importance. (See part 5.5.7 of the Atomic Absorption Methods section of this manual.)
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 2.5, 5.0 and 10.0 ug Cd/l, the standard deviations were ± 0.10 , ± 0.16 and ± 0.33 , respectively. Recoveries at these levels were 96%, 99% and 98%, respectively.

COBALT

Method 219.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01037

Dissolved 01035

Suspended 01036

Optimum Concentration Range: 5-100 ug/l

Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO₃.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO₃.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-900°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 240.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic

Approved for NPDES

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas but with reported lower sensitivity.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 3.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

COPPER

Method 220.2 (Atomic Absorption, furnace technique)

STORET NO. 01042

Dissolved 01040

Suspended 01041

Optimum Concentration Range: 5–100 $\mu\text{g}/\text{l}$

Detection Limit: 1 $\mu\text{g}/\text{l}$ _

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3 .

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3 .

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μl injection, continuous flow purge gas and non-pyrolytic

Approved for NPDES

Issued 1978

graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. Background correction may be required if the sample contains high dissolved solids.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as $\mu\text{g/l}$.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

LEAD

Method 239.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01051

Dissolved 01049

- Suspended 01050

Optimum Concentration Range: 5-100 $\mu\text{g/l}$

Detection Limit: 1 $\mu\text{g/l}$

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Lanthanum Nitrate Solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml conc. HNO_3 and dilute to 1000 ml with deionized distilled water. 1 ml = 50 mg La.
3. Working Lead Solution: Prepare dilutions of the stock lead solution to be used as calibration standards at the time of analysis. Each calibration standard should contain 0.5% (v/v) HNO_3 . To each 100 ml of diluted standard add 10 ml of the lanthanum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3 .
2. To each 100 ml of prepared sample solution add 10 ml of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-500°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure in the calculation see "Furnace Procedure", part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μ l injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, 71, May-June 1976.)
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
8. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as μ g/l.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 100 μ g Pb/l, the standard deviations were ± 1.3 , ± 1.6 , and ± 3.7 , respectively. Recoveries at these levels were 88%, 92%, and 95% respectively.

NICKEL
Method 249.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO₃.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO₃.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic

Approved for NPDES
Issued 1978

graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ZINC

Method 289.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01092

Dissolved 01090

Suspended 01091

Optimum Concentration Range: 0.2–4 $\mu\text{g}/\text{l}$

Detection Limit: 0.05 $\mu\text{g}/\text{l}$

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3 .

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solution for analysis should contain 0.5% (v/v) HNO_3 .

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2500°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 213.9 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Approved for NPDES

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipet tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/l.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

April 1977

NAQUADAT NO. 10605L

HARDNESS, TOTAL

(EDTA Titration)

Introduction:

In natural waters hardness is defined as a characteristic of water which represents the total concentration of calcium and magnesium ions expressed as calcium carbonate. Hardness is also caused by other polyvalent cations which seldom are present in more than trace amounts.

Principle:

Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Calmagite Indicator, which has a red colour in the presence of calcium and magnesium and a blue colour when the cations are sequestered.

Scope:

This method is applicable to surface and drinking waters and sewage and industrial wastes. The detection limit is 1 mg/l CaCO_3 .

Interferences:

Most polyvalent cations which normally interfere are either not present in natural waters in significant amounts or else are complexed by the addition of cyanide.

Excessive colour and turbidity interfere.

Reagents:

1. Univer - I - (Hach No. 206) - this is a registered trademark of the Hach Chemical Co., a commercially available reagent which contains Calmagite Indicator and sodium cyanide. Caution - this reagent is poisonous.
2. EDTA titrant (.01M) - dissolve 3.723 g disodium ethylenediamine tetraacetate dihydrate, also called (ethylenedinitrilo) - tetraacetic acid disodium salt (EDTA), $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ to 1 litre with distilled water. Standardize using the standard calcium solution.

3. Standard calcium solution (1000 mg/l CaCO_3) - weigh 1.000 g anhydrous calcium carbonate, CaCO_3 powder (primary standard, oven-dried at 105°C overnight). Add HCl slowly to dissolve the CaCO_3 . Add 200 ml distilled water and boil for a few minutes to expel the CO_2 . Cool, add a few drops methyl red solution and adjust to an intermediate orange colour by adding 3N NH_4OH or 1:1 HCl. Dilute to 1,000 ml with distilled water.
4. Buffer solution - dissolve 16.9 g ammonium chloride, NH_4Cl , in 143 ml concentrated ammonium hydroxide, NH_4OH . Add 1.25 g of magnesium salt of EDTA and dilute to 250 ml with distilled water.

Procedure:

1. Dilute 10 ml standard calcium solution to 50 ml with distilled water in a 100 ml beaker.
2. Add 1-2 ml buffer to give a pH 10.0 - 10.1 and stir well.
3. Add 1 scoop (1.0 g Univer - I dry powder and stir well).
4. Titrate with standard EDTA titrant to a completely blue end point within 5 minutes after addition of buffer.
5. Repeat using 50 ml sample (filter through a .45 μ filter membrane if the sample is turbid).

Notes:

1. Due to high pH titrate immediately after addition of buffer.

Calculation:

$$\text{Hardness as mg/l CaCO}_3 = \frac{A \times B \times 1000}{\text{ml of sample}}$$

A = ml titration for sample

B = mg CaCO_3 equivalent to 1.00 ml EDTA

$$= \frac{\text{vol of standard Ca solution}}{\text{vol of EDTA to titrate standard}}$$

Precision and Accuracy:

"A synthetic unknown sample containing 610 mg/l total hardness as CaCO_3 contributed by 108 mg/l Ca and 92 mg/l Mg, and the following supplementary substances: 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 250 $\mu\text{g/l}$ nitrite N, 1.1 mg/l nitrate N, 259 mg/l sulphate, and 42.5

mg/l total alkalinity (contributed by NaHCO_3) in distilled water was determined by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8% in 56 laboratories." (Std. Meth.)

References:

Std. Meth., 13th Ed., pp. 179-184.