A PASSIVE MONITOR FOR TRACE METALS IN WATER

By

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A Thesis

Submitted to the Faculty of Graduate Studies in Partial Fulfilment of the
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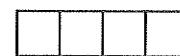
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A PASSIVE MONITOR FOR TRACE METALS IN WATER

BY

MARK ERROL MCCOMB

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

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ABSTRACT

A simple, inexpensive, passive monitor, based on a textile-bound polyacryloamidoxime chelating agent, was evaluated for the analysis of selected trace heavy metals in water using both Energy Dispersive X-Ray Fluorescence Spectroscopy and Wavelength Dispersive X-Ray Fluorescence Spectroscopy as a means of analysis.

It was shown that the preparation of polyacryloamidoxime cloth from the polyacrylonitrile precursor via reaction in methanolic hydroxylamine was controllable and reproducible. The capacity of the cloth for Cu(II) and Pb(II) was 1.12 and 2.17 mmol/gram respectively. It was shown that, in controlled *in vitro* laboratory experiments using a flow chamber, the sorption profiles of Pb(II) and Cu(II) were similar to those of chelating resins and fibres containing the amidoxime group. The rate of uptake of metals by the cloth was found to be dependent on the percent surface area converted to amidoxime groups, the concentration and type of metal being tested for, the time of exposure, the flow rate of solution and the temperature of solution. Distribution coefficients of $3.5*10^6$ and $1.5*10^6$ for Cu and Pb were observed. The average rates of uptake for Cu and Pb were 600 and 200

μg/gram/day (9.4 and 0.96 μmol/gram/day) respectively from dilute solution ([Cu] = 0.093 μmol/L, [Pb] = 0.014 μmol/L). From replicate samples, a relative error of < 10 % was observed for the sorption of Cu(II) and Pb(II). Experimental results of the first field tests involving passive monitoring of river water and lake water suggest that a number of ions can be identified and monitored simultaneously. The deployment of the monitors by the general public and the use of a mailing program was tested and shown to be feasible. These results indicate the feasibility of using polyacryloamidoxime cloth as a passive monitor for trace metals in water.

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I would also like to thank D. Williamson and C. Hughes of Manitoba Environment for their assistance and collaboration, as well as J. Tisdale of the Federal Environment for his assistance.

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Last of all, I wish to express my thanks and admiration to my wife Lori for her patience and understanding.

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1   INTRODUCTION / TRACE METALS IN THE ENVIRONMENT

The monitoring of trace metals in the environment has been a subject

of great concern over the last decade and will continue to be so as there are

ever increasing amounts of metals found in the environment. The sources

of heavy metals in the environment, and more specifically in water systems,

has been attributed primarily to man-made sources, such as waste discharge

and stack emissions from industrial sources and coal power production. The

amounts released are staggering, with values in the millions of tonnes per

year for a single metal.[1] This results in the subsequent contamination of

fresh water resources and an increasing accumulation of these toxins in the

human food chain.[2] Research over the last 20 years indicates that

consumption of heavy metals may be detrimental to a person's health at

levels lower than those which were once thought to be safe.[2-5] Thus, there

exists the need for the continuous monitoring of both fresh water supplies

and essentially all water sources, including the oceans, in order to better

understand the sources, transport and amounts of these toxic heavy metals.[6-8]

The level of heavy metals which can be found in the aqueous

environment can vary considerably depending on the location of sampling, time of year, etc. Most are found in trace amounts either in the mg/L range and more commonly sub mg/L range.[9-10] Depending on the location of sampling, whether ocean, river, fresh water, or ground water, a number of factors will dictate the form that the metal will be in as well as the type of matrix that surrounds it.[9,11-14] These factors will influence speciation of a metal, something which is critical in its measurement, as different forms have been linked to differing degrees of bio-availability and subsequent toxicity.[15] The matrix also plays a significant role, both by directly affecting the metal's speciation as in the case of high levels of humic material in water where a metal could be expected to be over 90 % bound to organic matter,[14] as well as affecting the ease of analysis, as in the case of ocean and sea water which can have a relatively high amount of a salt (alkali and alkaline earth metals) present.[16,17]

The most common method of water analysis today involves the collection of an aqueous grab sample from the location of interest followed by direct instrumental analysis at a dedicated central laboratory.[9,11,12] Although this has been satisfactory in the past for most types of analysis, it is practically impossible to monitor the amounts of a metal in a dynamic

aqueous system such as a river or lake by this means over an extended period of time. This would require a large number of grab samples, which is not practical from the view of human resources as well as being cost prohibitive. As well, a simple grab sample may not provide the best representative sample of the area to be tested at any one given time. If a concentration profile is required, several samples from around the area can be taken on one or more successive occasions to try and present a more accurate measure of the analyte in the area sampled.

The use of a passive sampler, a device that can measure the concentration of an analyte as a function of the time it is deployed, is one method that has been investigated in order to solve the aforementioned problem. Although, in the literature there exists a great deal of research on the passive sampling of organic compounds primarily in air and water, there is very little work being done with respect to the development of a means of passive monitoring of trace metals in an aqueous environment.

There are several significant benefits to the development of a passive monitor for trace metals in water. A passive monitor will allow the reduction in the cost per sample analyzed for many types of environmental monitoring and sampling, and allow for the direct application for the analysis

of many aspects of environmental pollutants. Fresh water supplies could be monitored continuously for trace metals thus ensuring quality of the fresh water supplies. Continuous monitoring of predetermined sites would allow for pollutant source identification over long term exposure and allow for the enforcement of pollution control guidelines. This could be applied in the cases of acid mine tailings, waste effluent and discharge from industry, as well as other sources. Transport phenomena of metals in water could be studied over short and long term time frames in an effort to improve various models of transport; as well the study of water pollution could be done with the aim to reduce human exposure to these pollutants.

These applications lead to the focus of this research, which was the investigation into the development of an effective passive monitor for trace heavy metals in water.

1.1   CURRENT METHODOLOGY

Sample collection starts in the laboratory well before the actual sampling takes place. The selection of clean and suitable sample containers is critical to ensure the validity of the analysis. More often than not, any error that is observed in an analysis starts with the actual sampling being

done; therefore, it can be said that sample collection is actually the most important part of any analysis.[18] Sample containers vary but ones made of glass and polymers, such as high density polyethylene and Teflon, are by far the most widely used and accepted.[18-20] In most cases sample containers can be used as received from the source. However, more stringent measures can be taken. For example, rigorous cleaning procedures can be adopted such as a 48 hour soak in 10% v/v HNO_3.[20] This ensures that sample contamination will not occur through leaching of metals from the container walls during storage.[18-21]

At the site of actual sampling a quantity of water is simply taken from the area of interest and placed in the sample containers. At this time a number of extra steps can be taken with regards to this initial sample before the actual analysis depending on the information which is wanted. These steps include sample filtration, addition of a preservative such as HNO_3, removal of interfering ions, pH adjustment, and sample preconcentration.[9,11,12,22]

Bulk filtration is used when the initial sample contains a large amount of humic material and/or other particulate matter. It may be necessary to remove this material, not only for analysis in which the particulate material

will most certainly interfere, but to ensure that the sample does not undergo any significant changes in speciation during storage. It has been observed that when sampling waters with large humic material content, the concentrations of metals in solution may actually increase during storage as they are subsequently leached from the humic material present in the sample.[23] To try and reduce such changes the sample is generally filtered with a 0.45 μm filter before storage.[24]

After the sample is collected and filtered if needed, it may be necessary to add a preservative to the sample to ensure that there is no sample loss on the container walls during storage, something which has been observed and commented about a great deal in the past.[18-21] Addition of the preservative, in most cases HNO_3, results in further complications. Any trace metals that were present in the sample in a labile form with a particle size < 0.45 μm will be extracted by the acid into the free ion and the net result will be a change in the speciation of the analyte in question.[23] Because of this the analysis of heavy metals may be conveniently broken down into two groups: total metals and dissolved metals.[16] Total metals are just that, the sample is digested completely in acid and the total metal concentration measured. As this digestion can be a time-consuming process, it is often the

case that only the dissolved metals are analyzed and reported. This is the metal content that is readily extracted from the fraction which passes through a 0.45 μm filter and is not necessarily in the free ionic form initially. The consolation to this oversimplification in analysis is that a correlation exists between the dissolved measured amount and toxicity in fish.[25]

After all of these steps, the sample is finally ready for storage and shipment back to a central laboratory for analysis of heavy metals, most likely by AA, GFAA, or ICP.[9,11,12,16] It is noted that in the laboratory a number of further steps may be taken with respect to the analysis, one of which is sample preconcentration.

The net result of all this is a sampling protocol for a single sample which is not only time consuming and costly, but which must be carried out by a skilled technician both at the location of sampling as well as in the laboratory. For multiple samples from a single location the time involved in sampling and the initial preparation steps can run into several hours or even days; the cost of this on a per sample basis can be excessive. This type of approach is hardly applicable if profile monitoring, pollutant source identification or transport modelling are to be done, in which a large number of samples must be gathered over an extended period of time.

1.2 SORPTION METHODS FOR SAMPLE PRECONCENTRATION

Sample preconcentration is perhaps the simplest and most effective method of lowering the detection limits in an analysis and may be defined as follows: "an operation (process) as a result of which the ratio of the concentration or the amount of the micro-components (trace constituents) and macro-components (matrix) increases".[28] Several general reviews have been written on this subject.[29-34] In the case of the analysis of aqueous samples, preconcentration generally refers to the removal of water from the analyte. When the analysis involves measuring the amounts of trace metals, preconcentration may also include separation of other matrix components such as organic matter including humic material, and the alkali and alkaline earth metals, both of which may interfere with the analysis.

One of the most common and accepted means of sample preconcentration of heavy metals is by means of an ion exchange or chelating resin.[32,35-39] By this method, an aqueous sample is filtered and then passed though the resin at a specific pH. The resin is chosen depending on the particular type of analysis. Only those metals which form stable complexes with the resin at the chosen pH are retained to any degree while other metals such as the alkali and alkaline earth metals are passed through

without being retained. After this the metals of interest can be washed off the column by adjusting the eluent pH to a suitable value, and then can be subsequently analyzed by various means. There are a large number of available chelating resins available and separation of any one metal from the bulk matrix and from each other is often possible.[32]

An extension of this approach is the use of a solid phase extraction sorbent in a form other than a column. These are based on a chelating agent bound either covalently to or adsorbed onto a solid material. As a vast number of different approaches to this method exist, as do the number of different type of materials which have been used to hold the chelating groups, only a few examples will be given here to inform the reader as to some of the general features of these sorbents. Polyurethane foam plugs with chelating agents adsorbed onto the foam have been used by a number of groups both in a column form[40,41] similar to that of an ion exchange column, and for an *in situ* means of metal collection.[42,43] Recently, a coated fused silica fibre was investigated as a means of solid phase micro extraction of metal ions from solution in a manner similar to the well documented SPME device used for organic analysis.[44] Use of small cartridges filled with a sorbent were used for the solid phase extraction of a number of

metals from solution, in a process similar to that of the chelating resins discussed above.[45] With all of these methods, analysis of the metals sorbed is done via acid extraction followed by traditional spectroscopic methods.

A slightly better approach is the use of a filter or membrane as a means of solid phase extraction. The advantage of this approach is that it can be coupled to a form of analysis which can measure the metals bound within the filter or membrane directly, without extraction. Glass fibres in the form of a disk,[46] as well as polymeric membranes,[47-51] and filters,[52,53] onto which chelating groups are covalently bound,[48,49] or adsorbed,[52,53] have been used to collect trace metals as the aqueous samples are filtered through them or deposited on them by electrochemical means[50]. Methods of analysis which do not require solvent extraction range from ESCA,[46,49] ASV[49], and NAA[51] to the slightly better XRF method, which will be discussed in detail later. The elimination of the extraction step results in a decrease in the time of analysis, a decrease in the cost of analysis and a reduction in the chance of sample contamination.

Preconcentration methods, although well established, possess several disadvantages over the direct analysis of a sample. The time of analysis is increased substantially because of the extra processing involved as the

majority of the preconcentration processes are mostly hands on and have not been automated. The use of solvents in the extraction process may result in sample contamination as well as an increase in the cost of analysis. The use of solvents will also lead to an increase in the amount of generated waste. Direct analysis of the filter or membrane types of solid phase extraction improves the analysis substantially as extraction is not required and, as will be shown later, constitutes an ideal starting point for a passive monitor.

1.3   X-Ray Fluorescence Thin Sample Methods

The use of X-ray fluorescence spectroscopy as a method of analysis of environmental samples containing trace heavy metals has gained considerable popularity over the last decade. This is primarily due to the advent of more sensitive and cost effective instruments as well as the implementation of newer sample preparation methods such as sample preconcentration, which extends the detection limit of XRF to the concentration range of metals found in the environment. XRF is a well established technique and the theory and applications have been thoroughly summarized in a recent text edited by Van Grieken.[54] A number of recent reviews are available which cover the background of this methodology and

recent applications.[55-58] While in the past traditional XRF methods dealt primarily with the analysis of powders or pellets, newer methods based on thin film analysis have shown that detection limits rivalling those of more traditional spectroscopic methods such as, AA, GFAA, and newer methods based on ICP, can be obtained with similar accuracy and precision in the analysis.[54] A short summary of some recent work and some of the inherent advantages and limitations to this approach of sample analysis are presented here.

In the case of the analysis of environmental water samples, XRF received little attention, as the direct analysis of an aqueous sample yielded relatively high detection limits primarily due to a large background produced from the water matrix itself. To overcome this problem, several methods of sample preparation and preconcentration were developed to introduce the analyte into the spectrometer without the water matrix. These range in sophistication, ease of use and analytical detection limits and may or may not be applicable to a given set of samples.[54,55]

Evaporation of the aqueous matrix and production of a pressed pellet or glass is one way to reduce the large background. However, this method is not without problems. A large amount of initial sample is required in

order to produce enough material for a pellet. Evaporation of this large volume of water requires extra steps in the analytical scheme, and extends the time of analysis considerably. In order to shorten the drying time, freeze-drying has been used successfully to some degree.[54] This requires the use of specialized equipment which may add to the cost and difficulty of the analysis. Evaporation to a powder may also result in sample inhomogeneity as well as allowing for the introduction of contaminants without the removal of possible interfering elements such as the alkali and alkaline earth metals.

Another method is the use of chelating resins in which the analyte is first concentrated onto the resin followed by the formation of a pellet from the resin itself.[54,55] In this method, the aqueous matrix is removed rather rapidly compared to the evaporative method. With the use of chelating resins, it is also possible to remove possible interfering elements such as the alkali and alkaline earth metals which may be present. However, as a pellet is still formed, there is the possibility of sample inhomogeneity. There is also the possibility of crystal formation within the glass pellet, something which can also interfere with the analysis.

Co-precipitation of the metals followed by formation of a pressed

pellet is also a widely used method.[54,55] Use of specific precipitating or chelating agents allows the selective preconcentration of an analyte in question, as discussed previously. This has proven to be useful, not only for the manufacture of a pellet, but has also been applied to thin film analysis in which a precipitate is collected on a filter paper and analyzed directly by the spectrometer.[54,55] One advantage is that an analyte can be selectively complexed, resulting in a higher degree of concentration relative to the matrix and other interfering analytes.

With pellets, or more specifically, samples of indeterminate or infinite thickness, accurate quantitation of an analyte can be extremely difficult. Matrix adsorption and enhancement effects result in over or under estimation of an analyte's concentration and require either multiple calibration curves with correction terms for different matrixes or carefully matched standards. Powerful software programs are usually required to analyze the sample and aid in the quantisation of the data. With a pellet there is also the underlying problem of sample inhomogeneity which again can lead to poor results.

In the case of thin samples, it is not necessary to implement such drastic measures, as the signal measured of any analyte is directly proportional to its concentration in the sample providing that the sample

layer is homogeneous. In fact, as the fluorescence intensities of all elements measured are based on a function of their atomic number (physical characteristics), it is possible to use one calibration curve for all elements in question and relate each concentration to a simple attenuation (correction) term. This readily simplifies and increases the accuracy and precision of analysis and allows for the use of an internal standard. The sensitivity is greatly increased as the background is reduced due to less scattering of incident radiation.

The collection of a precipitate or metal complex on or within a filter paper or membrane is perhaps one of the best methods for the analysis of aqueous environmental samples by XRF,[54] and a number of specific applications exist for samples ranging from atmospheric aerosols to ocean water samples.[54-57] There are some problems, however, with the collection of a precipitate on a filter or membrane. There is always a chance that there will be a loss of analyte through less than 100 % recovery, although this can be accounted for in standardization. Another problem is that filtration rates can be slow as filters can plug. There is also the possibility that the precipitate deposited on the filter will not be completely homogeneous in composition and particle size, something which can affect the analysis.

One method that was developed to overcome these problems was to introduce the metal complexing groups directly into a filter or membrane in order to form a completely homogeneous sample matrix.[54,55] In this method, an aqueous sample can easily be passed through the material and analyzed routinely with both accurate and precise results. This method, although now used extensively for the preconcentration and analysis of water samples by XRF,[54] still suffers from the fact that an aqueous sample must be collected. This limitation applies to all of the aforementioned XRF methods as they require an original aqueous sample.

1.4 PASSIVE SAMPLING

The method of passive sampling of an analyte involves the measurement of the concentration of the analyte as a weighted function of the time of analysis. In this way, the concentration of the analyte is integrated over the time of sampling. The principal advantage of this over the more traditional method of grab sampling is that only one device is necessary at a sampling location for the entire time of sampling. In the case of a grab sample, the number of samples collected over the same period of time may be large in order to gain the same time averaged information.

Another advantage of passive sampling is that it invariably involves an *in situ* method of measurement or sample collection. By this means the concentration of the analyte in question is measured in its native environment. There is no chance of a change in speciation or concentration of an analyte, which can often occur with a grab sample once it leaves the site of sampling, and the possibility of sample contamination is less likely. This can be critical, as in the case of trace heavy metal speciation in water, where the species of a given metal will more often than not determine its toxicity.[27]

Passive monitors for trace metals in water are not common and there appears to be very little research in this area. The reason for this is unknown but it is suspected to be simply due to a genuine lack of interest in developing this area of research.[59] The work has been predominantly geared towards *in vitro* experiments with very few actual field studies being done.

Passive monitoring of organic compounds both in air and water has been developed to a greater extent. Recent papers summarize the use of passive samplers for the analysis of compounds in air.[60,61] Much work has also been done to develop passive monitors for organic compounds in

water.[62-67]   Many different approaches have been taken: hexane filled dialysis bags,[62] solvent filled dialysis membranes,[63] semipermeable membrane devices,[64,65] a diffusive sampler,[66] and an activated carbon textile,[67] all of which range in complexity and ease of use.

There are several different approaches to *in situ* aqueous sample collection or measurement of trace heavy metals as a function of the time of analysis.[68] These vary considerably and include the following: collection of an aqueous grab sample at preset time intervals via mechanical devices in what can be considered a semi-continuous mode,[69-71] *in situ* collection and speciation via dialysis, again in a semi-continuous mode,[72-74] *in situ* measurement via electrochemical means as is the case with ion selective electrodes[75] and sample sorption preconcentration on a suitable sorbent.[42,43,47,48,76,77]

The use of a mechanical device which consists of a number of small individual sample chambers that are exposed to solution at preset time intervals, can be considered as a semi-continuous mode of monitoring and is not truly passive. The principle disadvantage to these devices is their inherent complexity which results in a high cost of manufacture and deployment and the sample produced is no better than a simple grab sample.

There is also the potential of sample contamination from the device. The possibility also exists of a change in the form of the analyte as the samples collected may be stored within the device for an extended period of time before extraction and analysis.

Various electrochemical means of *in situ* sample preconcentration and monitoring have been proposed. The simplest is the ion selective electrode. Use of these electrodes has not been favourable due to fouling of the electrode surface and the fact that the electrodes are ion selective and not ion specific.[75] Other electrochemical approaches are *in situ* sample analysis by stripping voltammetry,[78] and electrodeposition.[50] Again, the ease of fouling of the electrode surface has limited this area of research considerably. In any case, the inherent complexity of construction of such devices results in the fact that they are costly and therefore cannot be deployed in any great quantity. The fact that a potential must be applied to these devices essentially negates their classification as a truly passive monitor.

The use of dialysis bags, tubes and membranes are common approaches to the semi-continuous passive collection of both organic compounds and metals from solution. There has been some work in the past dealing with the use of dialysis as a means of passive monitoring of trace

metals. By this method only the metals which can pass through the dialysis membrane are collected. The result is a more accurate sample of what may be considered free or dissolved metals. The method is simplified by analyzing the dialysis solution directly.

One of the first papers approaching the subject involved placing a dialysis bag filled with pure water in the water to be sampled until equilibrium was established.[72,73] Analysis was done by neutron activation analysis and a comparison was drawn between the results of the dialysis collected samples and the dissolved fraction of metals measured from a 0.45 μm filtered grab sample. It was found that contamination of the dialysis bag, as well as the differing permeability of metals through the filter and the dialysis bag, resulted in poor results and that little correlation could be drawn between the two different samples.

The theory behind a modification of this early work was presented describing the addition of a sorbent inside the dialysis chamber.[73] By this means, only dialysable metals could pass into the chamber where they would subsequently be bound onto the sorbent, thus ensuring that the driving force of dialyses would be approximately constant for the uptake of metals by the device. The use of a sorbent also would result in the preconcentration of the

metals. It is not known whether or not this idea has been implemented.

Another early work used dialysis as a means of measuring free metals *in situ* in comparison with similar grab samples, some of which were analyzed immediately, and some of which had been stored for a length of time in polyethylene containers.[21] Analysis was done by NAA. It was observed that there was a measurable decrease in the amount of metal in solution after storage for one week. It was noted, however, that the dialysis was not carried out to equilibrium and there was no correlation drawn between the total metals found and the fraction of dialysable metals analyzed.

A recent paper evaluates dialysis as a means of *in situ* collection and speciation of heavy metals in water.[74] Several metals were studied from river water samples which were subsequently analyzed with GFAA. The rates of uptake of several metals were found to be dependent on not only the rates of transport through solution but adsorption onto the membrane as well. It was also observed that the equilibration time was dependent on the ionic strength of the solution and varied between 12 and 100 hours and thus would depend on sample location. As with previous studies it was observed that there was a significant amount of filterable metals (<0.45 μm) which were

not taken up by the dialysis device. Other contributing effects that were not studied but merely proposed to have an effect were water temperature, pH and the flow of water past the device. A significant problem with devices operating on the principal of dialysis, something which has been difficult to solve, is sample contamination both during manufacture of the dialysis device and during the actual sampling itself. The use of ultra pure water and dialysis material is needed if valid results are to be obtained.

In situ preconcentration by means of metal adsorption or chelation is perhaps the most promising method for the passive collection of an analyte in solution.[68] By this means heavy metals are simply sorbed by the monitoring device *in situ* and are subsequently analyzed by some means after exposure. There are two approaches to this method. In the first, the rate of uptake of a metal is known and the concentration sorbed can be measured as a function of the time of exposure. The concentration in solution can then be determined. The other involves the use of a sorbent which, when placed in solution, allows the establishment of an equilibrium of the metal between the sorbent and solution in a manner similar to that of the dialysis methods.

An early example of a passive monitor based on the principle of *in situ* sorption onto a solid support was presented by Gesser et al.[42] In this

work, polyester foam plugs were loaded with the chelating agent 1-(2-pyridylazo-2) naphthol before being exposed to a test solution containing ug/L concentrations of different metals, namely, Cu, Zn and Hg. As previous work with the passive uptake of organics from water showed that sorption onto the foam was primarily limited to the surface, a device was used to squeeze the foam plugs *in situ* in order to increase the exchange of water and hence amount of metal taken up. It was found that the amount of metal taken up was linear, in the case of Cu and Zn, with the number of squeezes, or in other words, the time of exposure. Deployment of such a device, however, was limited because of the mechanical nature of the squeezing apparatus. Another problem with this approach was that the actual analysis of the metals was done via a solvent extraction step from the foam followed by AA.

This work was later extended to the analysis of Cd.[43] Both foam plugs, as used previously,[42] and foam strips were investigated with the foam plugs performing similarly to the previous work. The foam strips did not use any mechanical means for water and hence metal distribution and were found to saturate relatively quickly compared with the plugs. This work was repeated with the foam strips and the amount of Cd taken up was observed

to increase with the time of exposure, however, the relationship was not strictly linear.[76] It was proposed that because the time of exposure was relatively long and that the chelating agent was not covalently bound to the foam, the chelating agent desorbed from the foam strip into solution.

The use of proton-induced X-ray emission (PIXE) analysis of ion exchange membranes was another early attempt at the development of a passive monitor for trace metals.[47] A commercially available membrane was tested both in the laboratory and in a river for its ability to take up metals. The method used was very simple and consisted of exposing the membrane to solution followed by direct analysis by PIXE. The primary advantage of this was that solvent extraction was not necessary for analysis of the ions adsorbed. Although detection limits for Pb were proposed to be 0.1 ppb, it was found that equilibration times were relatively long at 80 hours and that the membrane used possessed a relatively high affinity for the alkali and alkaline earth metals thus decreasing its total capacity for the heavy metals of interest.

Recently a device loaded with a solid sorbent was reported for the analysis of diffusible ions in soil ground water and other aqueous systems.[77] This device consisted of a rigid spherical shell over which is attached a

freely permeable fabric or mesh. The interior of this device is filled with an ion exchange material or other desired sorbent. For the analysis of heavy metals it was proposed that the device be loaded with one of any number of the hundreds of commercially available chelating resins such as Amberlite IRN-150. The entire device could then be deployed for a fixed amount of time in the area to be sampled. Collection of ions would be dependent on their ability to diffuse into the device and their relative stabilities on the sorbent. Although this approach is one of the best to date, it suffers from the fact that the device is still inherently complex to construct and the analysis of the metals taken up would not be straight forward. It is unknown if this device has actually been evaluated in the field.

1.5   GOALS OF THIS RESEARCH

The goal of this research was the development of a passive monitor for the analysis of trace heavy metals in water. From the previous discussion on current sampling methodology, solid phase sample preconcentration, XRF analysis of thin samples and previous work regarding the development of passive monitors, a number of criteria were selected which were deemed necessary for the proper design of an effective passive monitor.

The monitor should be easy and inexpensive to manufacture, easy to deploy even by an untrained lay-person, small enough that it can be mailed inexpensively to and from a remote location, sensitive to the heavy metals which are to be analyzed, and insensitive to interfering matrix components such as humic material and the alkali and alkaline earth metals. The method of analysis chosen must be easy and inexpensive and, preferably, without any in-laboratory sample pretreatment or extractions before analysis. Other factors which were considered desirable were the ability to withstand an indefinite storage time before analysis without any change in the speciation or concentration of the metals sampled as well as some form of sample preconcentration in order to increase the sensitivity of analysis.

Consequently, a device was constructed which consisted of amidoxime chelating groups covalently bound to polyacrylonitrile textile. The amidoxime chelating group was chosen for a number of reasons, one of which was its ability to chelate a large number of different heavy metals without taking up alkali and alkaline earth metals.[79] Another factor in this choice was the great amount of work that has been done in the past with regards to using the amidoxime group for the preconcentration and analysis of trace metals in water.[80-125] The choice of a textile as a solid polymeric

support for the chelating agent was decided upon based on previous work with amidoxime containing fibres.[80-99]

Deployment of this chelating cloth was done by encasing it in a common 35 mm slide holder. The idea for this came from previous work in this laboratory with regards to passive monitors for organic compounds in air and water.[61,67] Placement of this device in the water to be analyzed resulted in the uptake of heavy metals by the chelating groups. The net result may be considered a method of *in situ* sample preconcentration.

After removal of the sampler from water, the metals taken up were directly analyzed both qualitatively and quantitatively with XRF via the thin sample technique. Radioisotope source EDXRF spectroscopy was chosen as the method of analysis as it provides for relatively sensitive, simultaneous multi-elemental analysis, while avoiding costly and time consuming solvent extraction. Wavelength dispersive XRF spectroscopy, with a sensitivity of about 10^6 over that of the radioisotope source EDXRF was also investigated as a means of analysis of the samplers.

28

EXPERIMENTAL

2   INTRODUCTION

The experimental part of this research was roughly divided into three separate areas of investigation. In the first part, the actual process of manufacturing the passive monitors was developed. This involved the investigation of some of the properties of the polyacrylonitrile cloth, optimizing the conversion of nitrile groups to amidoxime groups on the cloth to be used in the monitors, and investigating some of the physical properties of the converted cloth.

The second part of this work involved the *in vitro* testing of some of the physical properties of the cloth with respect to the uptake of metals from solution. This included testing the monitors with respect to the rates of uptake of metals from a flowing solution similar to that which would occur in a river or lake setting. In addition, a number of factors affecting the sorption of metals from solution were investigated in a series of controlled batch experiments.

The third part of this research involved the limited field testing of the monitors. This was done in order to evaluate the capability of chelating

Orlon cloth as a passive monitor for trace metals in water. Several different locations were chosen which had water of varying flow rates and turbidity.

2.1   REAGENTS

Metals used in the *in vitro* tests and in standard solutions were prepared from the nitrate salts and were reagent grade. Reagents used in the conversion of the nitrile groups on polyacrylonitrile cloth to amidoxime chelating groups, $NH_2OH*HCl$, NH_4OH, NaOH, and ethanol (95%) were reagent grade while methanol (100%) used was electronic grade. Reagents used in the treatment processes of the cloth were NaOH and NH_4OH, reagent grade, and HCl, spectroscopic grade. Samples, solutions and standards used in AA were prepared in reagent grade HNO_3, while those used in GFAAS were prepared in environmental grade HNO_3.

Water used for the *in vitro* tests in the flow chambers was derived from reverse osmosis feedstock (ro). Water used in the standards for GFAA, and in the conversion process, was further purified by passage through a 4 stage Barnsted Nano-Pure II purification system (ro, nanopure).

Filters used in the field tests were 0.45 μm cellulose acetate type HA manufactured by Millipore and # 1 Fine manufactured by Whatman. The

film used in the preparation of samples for λDXRF spectroscopy was 6.3 μm X-ray polypropylene film supplied by Chemplex Industries Inc., NY. USA.

2.2   APPARATUS

During the course of this research, several pieces of apparatus had to be constructed to be used in conjunction with other standard laboratory apparatus. This was done in order to investigate the physical characteristics of the passive samplers and the dynamics of the uptake of ions from solution. The apparatus manufactured in the laboratory is listed here.

For the conversion process a batch reactor was made using a rectangular glass tank placed in a constant temperature circulating water bath. Stirring was provided by a glass stirring rod. A diagram of the batch reactor is shown in Figure 1.

For the *in vitro* experiments, a constant flow chamber was set up in which the monitors could be placed. This consisted of a 200 Litre plastic barrel, a small immersible mechanical pump, glass and silicon rubber tubing, a glass flow chamber (height ~30 cm, diameter ~10.6 cm) with a plastic stopcock and overflow and a plexiglass top for the barrel. The flow rate was set at ~ 4.75 Litres/ minute with an average linear velocity in the chamber
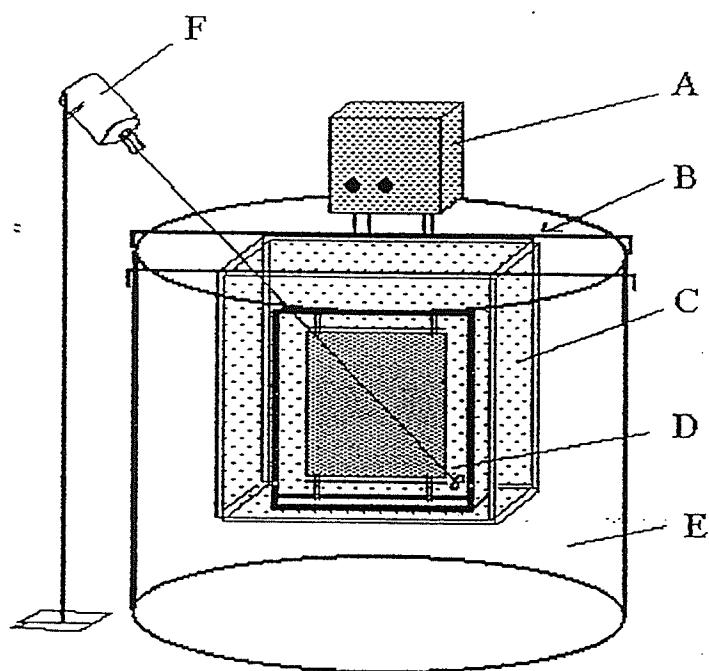
Figure 1.   Diagram of the Batch Reactor.
A. Circulating water heater, B. Wire frame, C. Vertical tank
D. Glass stirring rod, E. Reservoir, F. Motor.

of 51.8 cm/ minute. A diagram of the flow chamber and a sample holder is shown in Figure 2.

For the *in vitro* experiments with variable flow rates, a second series of constant flow chambers was added to the original flow chamber. This series consisted of 4 flow chambers (height ~12 cm, diameter ~ 9 cm) within each of which a monitor could be placed. Each flow chamber was connected to a different diameter glass tube which was used to achieve the different flow rates of 0.08, 0.6, 11, and 15 cm/ minute. This flow chamber was placed on top of the 200 Litre barrel and the water flowing through each individual cell was allowed to drain directly into the barrel. A diagram of the multiple flow chamber and the sample holder is shown in Figure 3.

A flow chamber with a modified sample holder was constructed for the investigation into the effects of desorption of metals from the cloth into solution. A glass flow chamber (height ~ 20.3 cm, diameter ~ 9 cm) similar to the one described previously was used. A direct feed of water (ro) was used to ensure a fresh supply of water during the course of the experiment. The flow rate was set at ~ 1.3 Litres/ minute with an average linear velocity in the chamber of 20.3 cm/ minute. The sample holder was designed to hold all of the samples in approximately the same proximity to the sides of the
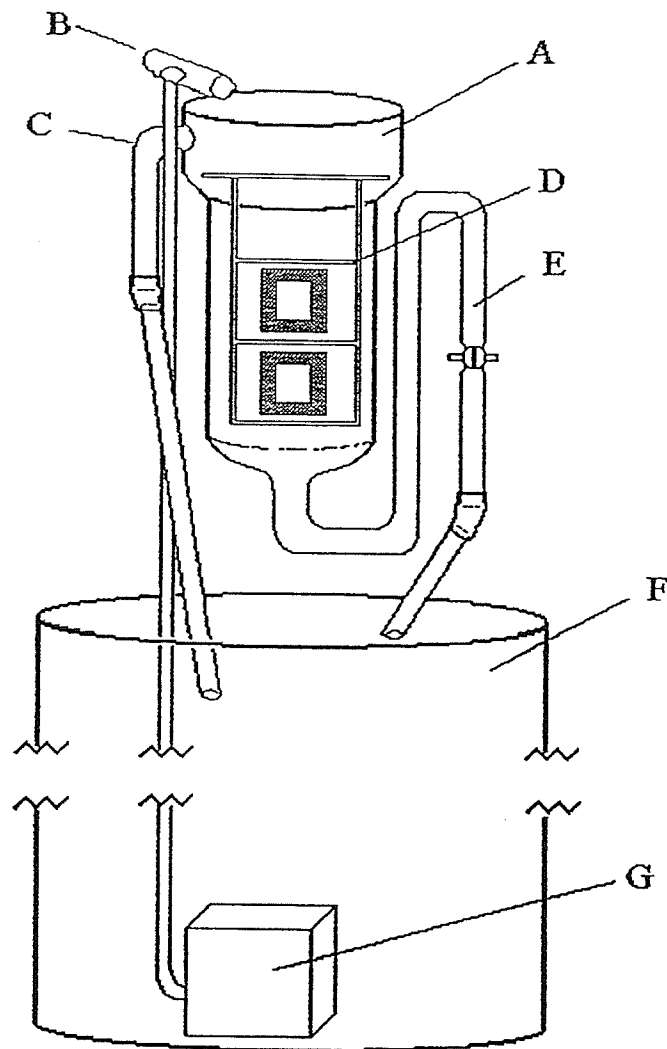
Figure 2.   Diagram of the Flow System.
A. Flow chamber, B. Water inlet, C. Overflow
D. Glass rack with monitors, E. Drain with stopcock
F. Reservoir, G. Submersible pump.
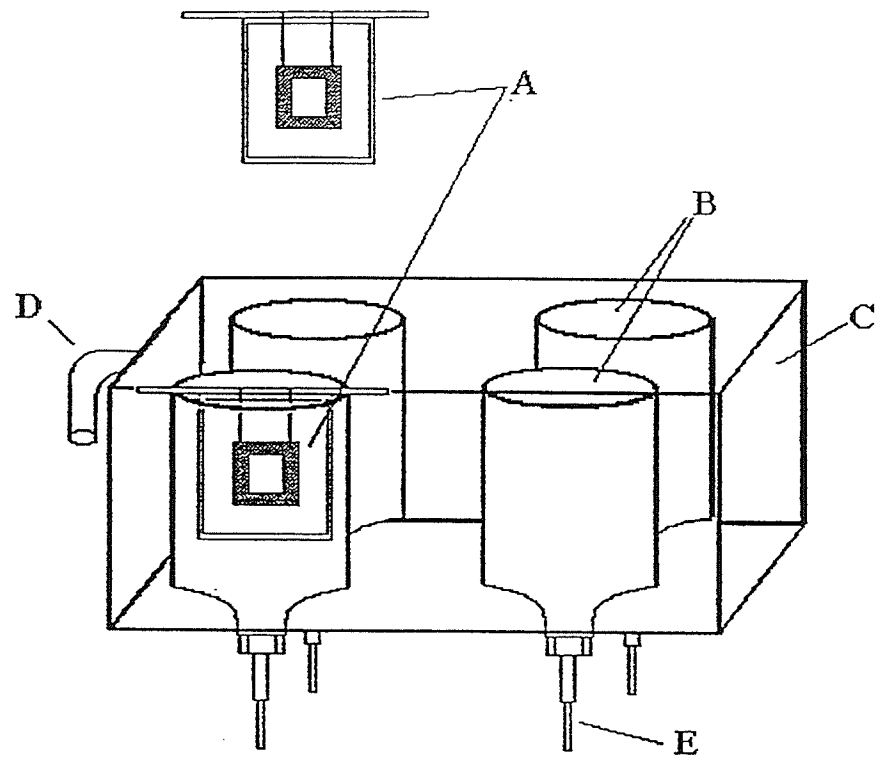
Figure 3. Diagram of the Multiple Flow System.
A. Glass rack with monitor, B. Individual flow chambers
C. Enclosed container, D. Overflow
E. Glass tubing of variable diameter.

flow chamber to try and minimize the effects of turbulence. As well, the turbulence in the flow chamber was minimized by suspending a plastic petri dish with holes placed in it above the samples. The effect of turbulence was tested with a dilute solution of K_2CrO_3 which was added drop-wise to the chamber. A diagram of the flow chamber and modified sample holder is shown in Figure 4.

2.3   INSTRUMENTATION

Several different methods were used in this research for the analysis of the metals taken up by the cloth from solution. These included both Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) and Wavelength dispersive X-Ray Fluorescence Spectroscopy (λDXRF) which were used to analyze the metals on the cloth directly. As well, Atomic Absorption Spectroscopy (AA) and Graphite Furnace Atomic Absorption Spectroscopy (GFAA) were used to analyze the metals extracted from the cloth and the metals found in solution. The instruments and methods are described later in more detail.

An ORION Expandable IonAnalyzer EA 940 was used for the measurement of solution pH. Infrared spectra were recorded on a Bomen,
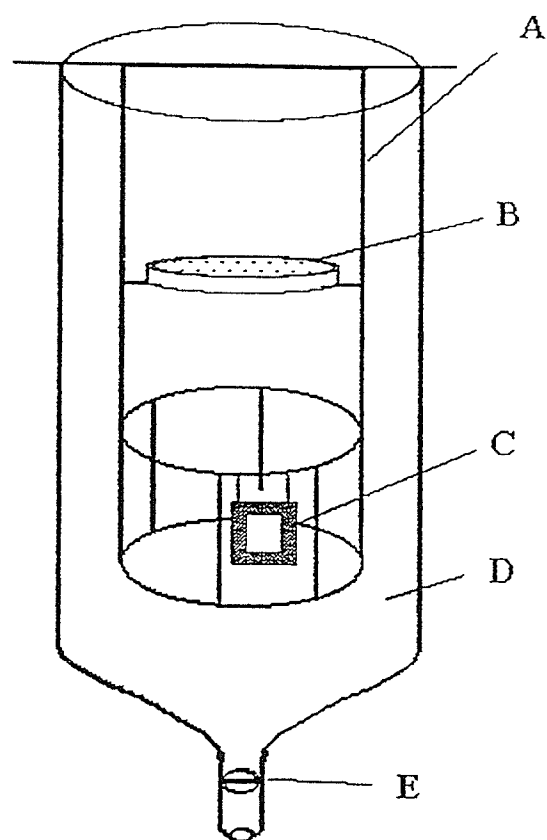
Figure 4.   Diagram of the Flow Chamber used for Desorption.
A. Glass rack with monitor, B. Petri dish with holes
C. Monitor, D. Flow chamber, E. Stopcock and drain.

Hartmann, Brawn, Michelson MB Series, Fourier Transform Infrared Spectrometer (FTIR), details of which are given later.

2.3.1 RADIOISOTOPE EDXRF SPECTROSCOPY

An EDXRF spectrometer, consisting of an annular 0.5 Ci ^{241}Am source, a New England Nuclear Si(Li) semiconductor detector, a Nuclear Semiconductor 512 amplifier, and a Tracor Northern TN 1705 pulse-height analyzer, was used to measure the amount of metals taken up by the monitors after exposure to both the *in vitro* test solutions and the river and lake waters. The cloth samples or passive monitors were placed on a specially constructed sample holder which was set at fixed optimum height above the detector of the EDXRF spectrometer.[126] A diagram of the sample holder, source and detector configuration is shown in Figure 5.

The intensity of the resulting fluorescence of different metals was found to be linear with respect to time of spectral acquisition. An arbitrary time of 3000 seconds for data acquisition was chosen for sensitivity and convenience. Peak integration was done using the software supplied with the spectrometer. Spectrum plotting was done by converting the resulting spectrum into MathCad using a program written in QUICK BASIC. A copy
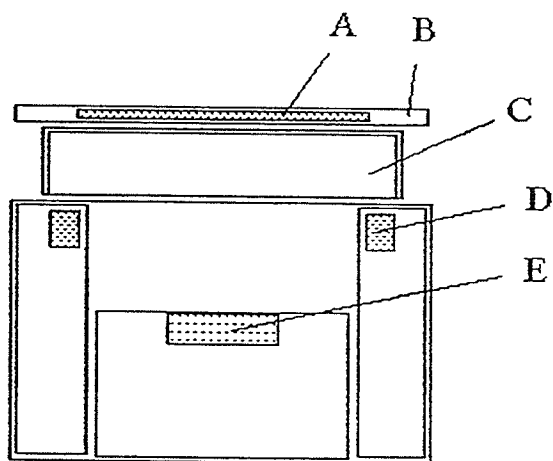
Figure 5.   Diagram of the Sample Placement on the EDXRF Detector.
A. Cloth encased in the monitor, B. Body of the monitor
C. Plastic sample holder, D. Annular source, E. Detector.

of the QUICK BASIC software program can be found in Appendix 1. Representative blanks were recorded for all samples. Several spectra were recorded for various metals in order to aid in the qualitative analysis and are given in Appendix 2.

2.3.2 WAVELENGTH DISPERSIVE XRF SPECTROSCOPY

Wavelength dispersive XRF spectroscopy was also used as a means of analysis of the cloth samples and monitors. An American Research Laboratories spectrometer with a 50 sample capacity auto-sampler was used. The spectrometer was located at AECL Pinawa, MB. Spectra were recorded with the assistance of the technical staff.

Analysis of the monitors was carried out on the cloth samples after removal from their plastic frames. The cloth pieces were then placed on a cardboard backing followed by encasement in 6.3 μm polypropylene film. This small packaged sample was then placed in the supplied XRF sample holders. A diagram of the cloth sample and sample holder is shown in Figure 6. Spectral acquisition was done using the parameters given in Appendix 3. Representative blanks were recorded for all analysis.
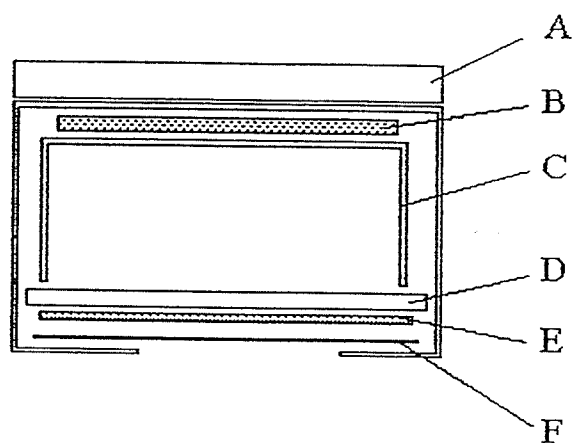
Figure 6.   Diagram of the Sample Placement in one of the Sample Cups
used with the λDXRF Instrument.
A. Cover, B. Spring, C. Plastic ring, D. Cardboard backing
E. Cloth removed from the monitor, F. Polypropylene film.

2.3.3 AA SPECTROSCOPY AND GFAA SPECTROSCOPY

Analysis of the solutions used in batch experiments, extracted metals from cloth samples and the test solutions used in the flow chamber apparatus, were carried out using a Varian SpectrAA-20 Atomic Absorption Spectrometer equipped with a Varian GTA-96 Graphite Tube Atomizer and an auto-sampler. Quantitation of the XRF results was carried out by extraction of selected samples followed by AA or GFAA analysis. Standards were prepared by serial dilution of stock 1000 mg/Litre standard solutions. Solutions for GFAA were adjusted to 0.5 % HNO_3 (v/v). Solutions for AA were adjusted to 5% and 20 % HNO_3 (v/v).

2.4 QUANTITATION PROCEDURE

For the quantitative analysis of metals sorbed onto the cloth, both EDXRF and λDXRF were used in conjunction with AA and GFAA. Quantitation of the metals bound to the cloth, as determined by XRF, was carried out from calibration curves obtained from the extraction of metals from a few of the samples followed by AA or GFAA analysis. Calibration curves can be found in Appendix 4.

Extraction of the metals from the cloth was done via a batch process using a fixed amount of either 0.5%, 5% or 20% (v/v) HNO_3 in water depending on the amount of metal bound to the surface of the cloth. Three extractions were necessary for the quantitative extraction of the metals bound to the cloth. These were then combined to a fixed volume suitable for AA or GFAA analysis. Results from one of the extractions performed, showing the degree of extraction, are given in Appendix 5.

PREPARATION OF CHELATING ORLON CLOTH

3   GENERAL PROCEDURE

The preparation of the passive monitors began with the conversion of the nitrile groups on the surface of the polyacrylonitrile cloth to amidoxime groups via the reaction in methanolic hydroxylamine as described by Lin.[111] The reaction is depicted below in Scheme 1.

$$\left(-CH_2-\overset{|}{CH}-C\equiv N\right)_n + NH_2OH \longrightarrow \left[-CH_2-\overset{|}{CH}-C\overset{\nearrow NOH}{\underset{\searrow NH_2}{}}\right]_n$$
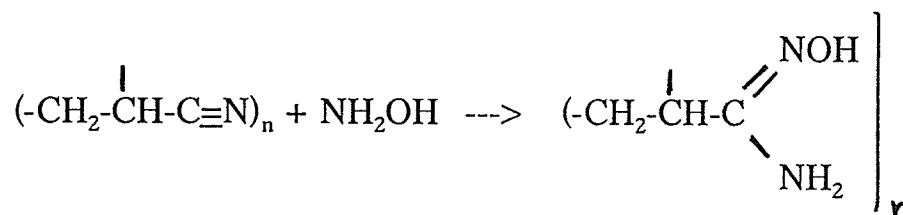
Scheme 1. Reaction of a polyacrylonitrile monomer unit with hydroxylamine to produce polyacrylamidoxime.

The method of conversion was based on the literature method used for the treatment of polyacrylonitrile staple fibres and thus was not directly applicable to the conversion of the textile.[81,127] The reason for this is that the textile is made up of thread woven from the staple fibre and thus possesses its own physical properties, an extension of those of both the thread and the fibre.

Orlon cloth (polyacrylonitrile) was obtained from Test Fabrics Inc. and used as received.[128] The physical properties of the supplied cloth are given in Appendix 5. General properties of polyacrylonitrile fibers, the precursor to the woven thread and thus the cloth, are given in Appendix 6. Cloth pieces were cut from the supplied material and the edges fused with a flame heated stainless steel spatula. After this, opposite ends of the cloth were sewn, using cotton thread, around a frame in order to expose the entire surface area of the cloth to the hydroxylamine solution. A glass frame constructed from ~4 mm glass rod was used as the support, with the exception of the first two batches of cloth produced, in which a Ni frame was used. Diagrams of the arrangements are shown in Figures 7, 8 and 9.

Solutions of hydroxylamine in 50% methanol/water or 50% ethanol(95%)/water (v/v) were prepared by adding a fixed amount of $NH_2OH*HCl$ with an equal molar amount of NaOH or NH_4OH to water, pH = 7, followed by the addition of methanol or ethanol. Conversion was done via a batch process by exposing the pieces of cloth to the hydroxylamine solution. Both horizontal tank and vertical tank arrangements were used for the conversion process.
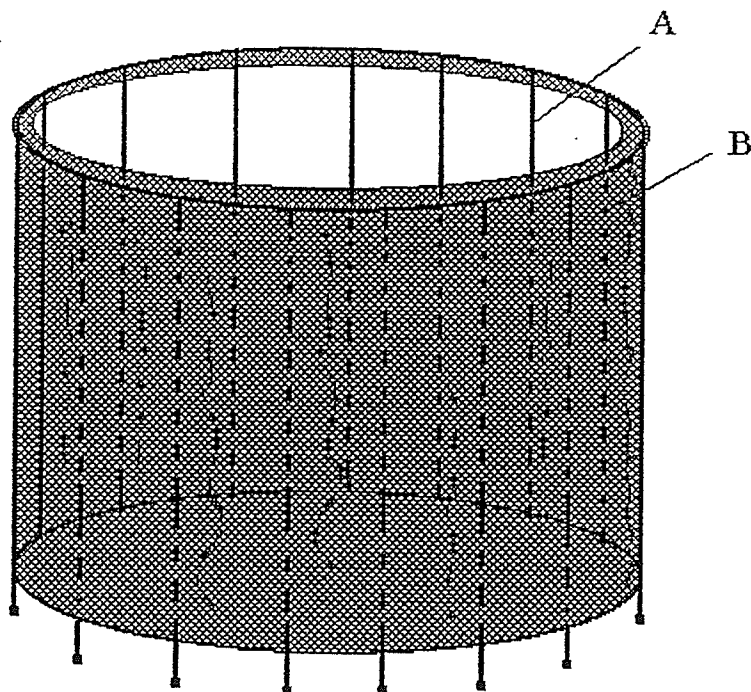
Figure 7.   Diagram of the Ni Wire Frame with Cloth.
A. Ni wire frame, B. Cloth.
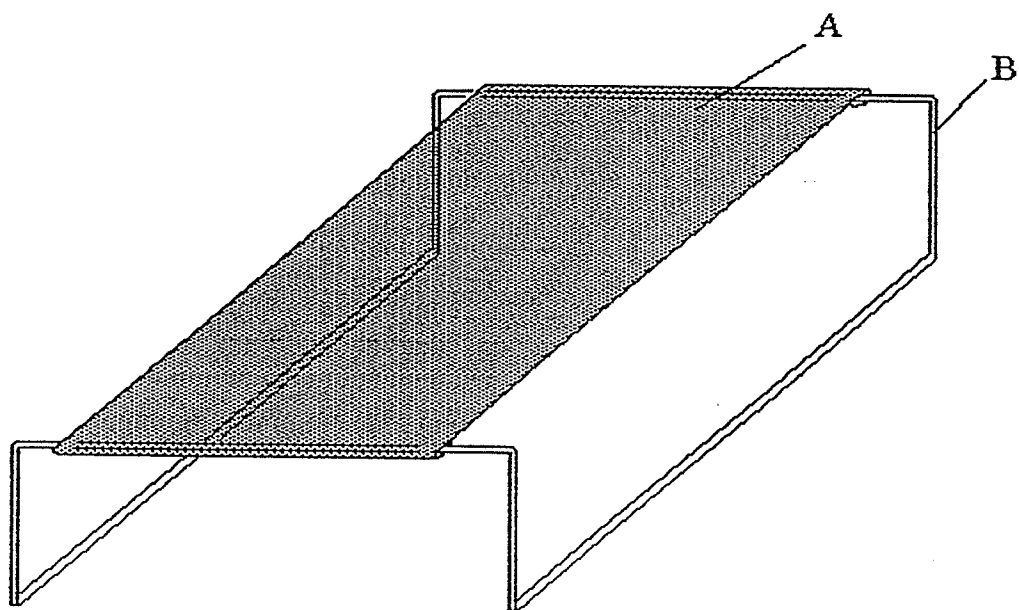
Figure 8.   Diagram of the Glass Frame and Cloth used in the Horizontal Tank.
A. Cloth, B. Glass frame.
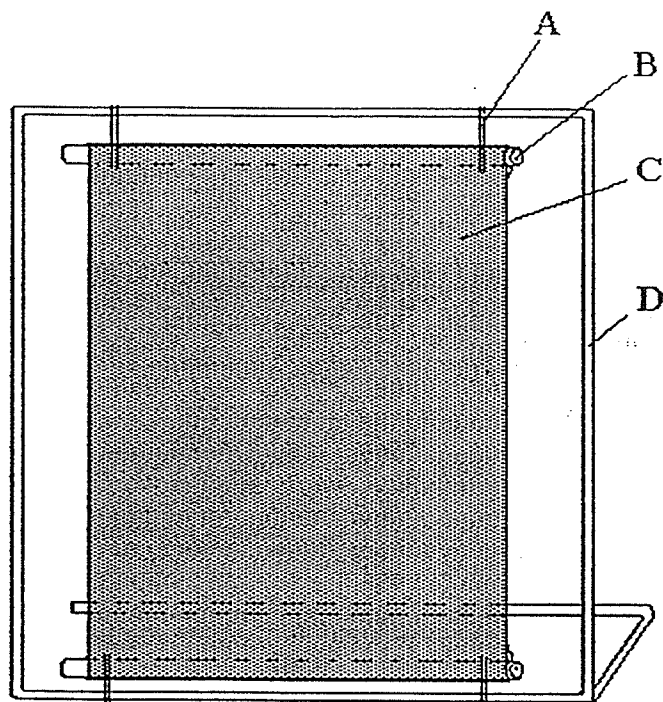
Figure 9. Diagram of the Glass Frame and Cloth used in the Vertical Tank.
A. Cotton thread, B. Glass rods, C. Cloth, D. Glass Frame.

For the first two attempts involving the conversion of the cloth, a 1000 mL beaker was used as a vertical reaction vessel. The Ni wire frame was placed in the beaker along with the hydroxylamine solution and placed on a hot plate with a built-in magnetic stirrer. Stirring was provided by a Teflon covered stirring bar. The beaker was covered with Saran wrap to prevent excessive evaporation during the coarse of the reaction.

The horizontal conversion was carried out by laying the glass rack in a Pyrex container which was heated by two hot plates with built in magnetic stirrers. The tank was covered with Saran wrap to prevent excessive evaporation. Stirring was provided by two Teflon coated magnetic stirring bars, one placed on each hot plate.

Two different designs were used in the vertical conversion process. The first was a rectangular glass tank placed on a hotplate. As the bottom surface of the tank was uneven, a shallow tray of sand was used to ensure even heating of the bottom of the glass container. As before, Saran wrap was used to cover the top of the tank. A glass stirring rod was used to ensure solution mixing.

A second more elaborate set-up was also used which allowed better control of the temperature of the reaction. In this case, the rectangular glass

tank was placed in a constant temperature circulating water bath. Stirring was provided by a glass stirring rod and the top covered in Saran wrap. A diagram is shown in Figure 1.

After conversion the cloth was washed with water (ro) and allowed to dry on the frame to prevent excessive shrinkage. During the later course of this research (batches 28-35) the cloth was removed from the glass frame and suspended from a rack which also prevented the cloth from shrinking excessively. After drying in air, the cloth was transferred to a desiccator and dried under vacuum and in the case of later produced cloth (batches 28-35) dried in a vacuum oven at 65 °C. A total of 35 batches of cloth were manufactured using this batch process. Reaction conditions for each batch of cloth, the type of tank used, the degree of conversion and general observations are given in Table 1.

After the conversion process was complete, small pieces of the amidoxime containing cloth were cut into 2 x 2 cm^2 squares for use in both the flow and batch laboratory experiments. As well, 3.5 x 4 cm^2 pieces were cut and placed into standard 35 mm slide holders to produce the passive monitors. The ends of all the cloth pieces cut were fused with a hot spatula to prevent fraying. A picture of a passive monitor is shown in Figure 10.

TABLE 1: Properties of the amidoxime containing cloth.

Batch #	Mass Cloth (grams)	Mass NH_2OH *HCl (grams)	Tank[1]	Base[2]	Solvent[3]	Conditions	%[4]	Cloth Properties
1	6.26	63.1	Ni	NaOH	MeOH	45 oC x 48	10	soft, yellow
2	6.92	3.0	Ni	NaOH	MeOH	45 °C / 5 days	7	soft, white
3	6.84	20.0	H	NH_4OH	MeOH	45 °C x 29 hours 60 °C x 2 hours	50	soft, beige
4[5]	6.81	from batch 3	H	NH_4OH	MeOH	90 °C x 4 hours 20°C x 3 hours	70	brittle, yellow
5[5]	7.07	from batch 3	H	NH_4OH	MeOH	80°C x 2 hours 45°C x 24 hours	28	stiff, yellow
6	6.72	6.05	V.1	NaOH	EtOH	40°C x 10 hours 60 °C x 4 hours	7	soft, yellow
7[5]	6.48	from batch 6	V.1	NaOH	EtOH	65 °C x 24 hours	22	soft, yellow
8	5.87	6.0	V.1	NaOH	EtOH	65 °C x 7 hours	30	soft, beige
9	5.69	20.04	V.1	NH_4OH	MeOH	43 °C x 8 hours 70 °C x 39 hours	11	soft, beige
10	6.36	29.61	V.1	NH_4OH	MeOH	65 °C x 24 hours	16	soft, beige

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TABLE 1: Properties of the amidoxime containing cloth.

Batch #	Mass Cloth (grams)	Mass NH_2OH *HCl (grams)	Tank[1]	Base[2]	Solvent[3]	Conditions	%[4]	Cloth Properties
11	5.34	40	V.1	NH_4OH	MeOH	65 °C / 24 hours	14	soft, yellow
12	6.28	30	V.1	NH_4OH	MeOH	85 °C / 22 hours	90	brittle, yellow
13	6.81	30	V.1	NH_4OH	MeOH	60 °C x 48 hours	62	soft, yellow
14	5.77	30	V.1	NaOH	MeOH	68 °C x 14 hours	14	brittle, yellow
15	5.75	30	V.1	NaOH	MeOH	64 °C x 2 hours 74 °C x 2 hours	57	stiff, yellow
16	5.53	30	V.1	NaOH	MeOH	60 °C x 4 hours	5	soft, white
17	4.98	30	V.2	NaOH	MeOH	65 °C x 24 hours	100	brittle, white
18	3.59	30	V.2	NaOH	MeOH	65 °C x 7 hours	48	soft, beige
19	3.57	30	V.2	NaOH	MeOH	43 °C x 8 hours 70 °C x 39 hours	30	soft, white
20	2.28	60	V.2	NaOH	MeOH	65 °C x 24 hours	44	soft, white

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TABLE 1: Properties of the amidoxime containing cloth.

Batch #	Mass Cloth (grams)	Mass NH$_2$OH *HCl (grams)	Tank[1]	Base[2]	Solvent[3]	Conditions	%[4]	Cloth Properties
21	3.06	60	V.2	NaOH	MeOH	54 °Cx15.7 hours	84	brittle, white
22	3.09	60	V.2	NaOH	MeOH	55 °C x7.7 hours	14	soft, white
23	2.90	60	V.2	NaOH	MeOH	54 °C x12.3hours	46	soft, white
24	2.93	60	V.2	NaOH	MeOH	55 °Cx10.3 hours	21	soft, white
25	5.15	60	V.2	NaOH	MeOH	55 °C x 12 hours	73	flexible, white
26	4.88	60	V.2	NaOH	MeOH	55 °C x 12 hours	42	soft, white
27	4.85	60	V.2	NaOH	MeOH	56 °C x 12 hours	47	soft, white
28	4.80	60	V.2	NaOH	MeOH	54 °C x 12 hours	47	soft, white
29	4.83	60	V.2	NaOH	MeOH	54 °C x 12 hours	(6)	damaged
30	4.85	60	V.2	NaOH	MeOH	54 °C x 12 hours	47	soft, white

TABLE 1: Properties of the amidoxime containing cloth.

Batch #	Mass Cloth (grams)	Mass NH$_2$OH *HCl (grams)	Tank[1]	Base[2]	Solvent[3]	Conditions	%[4]	Cloth Properties
31	4.90	60	V.2	NaOH	MeOH	54 °C x12 hours	52	soft, white
32[5]	4.93	60 +batch 31	V.2	NaOH	MeOH	55 °C x12 hours	100	stiff, white
33	4.85	60	V.2	NaOH	MeOH	55 °C x26 hours	100	brittle, white
34	4.92	60	V.2	NaOH	MeOH	55 °Cx21.3 hours	100	brittle, white
35	4.94	60	V.2	NaOH	MeOH	56 °Cx12.3 hours	63	soft, white

1) Tank used: Ni = Ni rack in a 1000 ml beaker
             H = horizontal tank, V.1 = vertical tank 1, V.2 = vertical tank 2. (glass racks)
2) Base: solution adjusted to pH = 7
3) Solvent used with water, 50 % (v/v), EtOH = ethanol (95%), MeoH = methanol
4) Degree of conversion in %, see text for formula.
5) Hydroxylamine solution reused from previous batch.
6) Cloth damaged while drying at 120 °C for 5 minutes
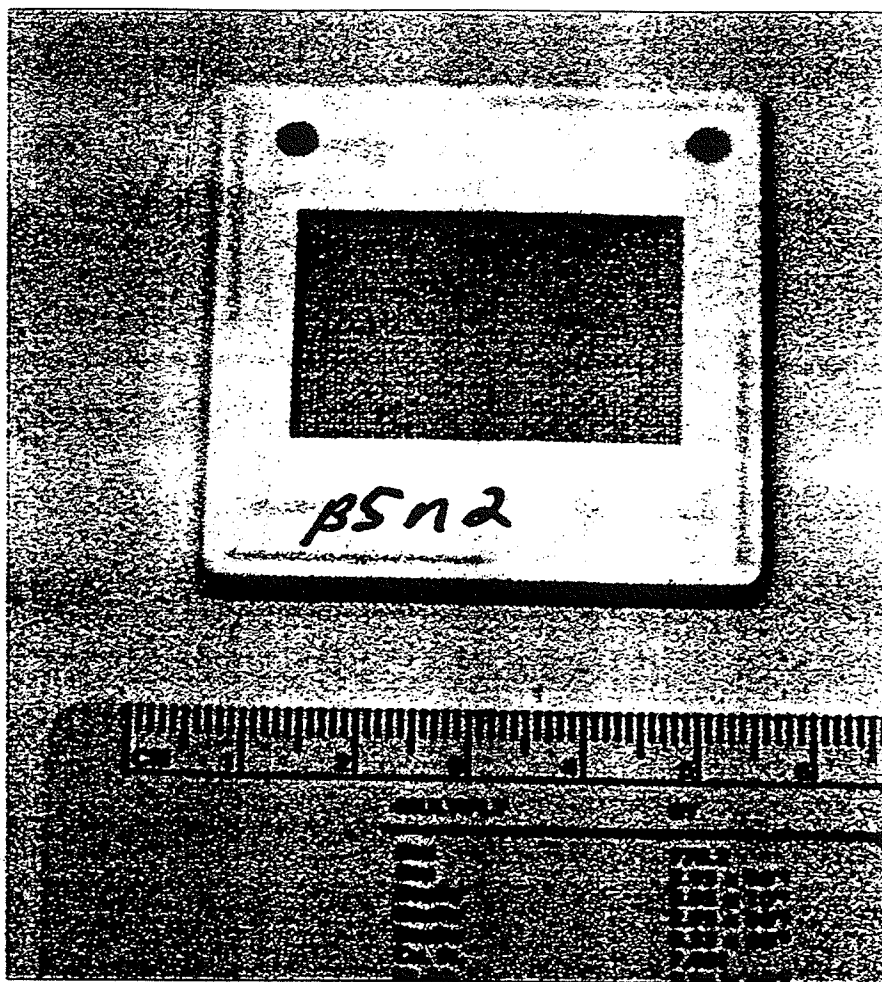
Figure 10.   Photograph of a Passive Monitor.
A.   35 mm plastic slide frame, B. Amidoxime chelating cloth.

In order to quantify the effect of the different reaction conditions on the degree of conversion of nitrile groups to amidoxime groups, the cloth was weighed before and after the conversion process. The % conversion, a measure of the degree of conversion, was calculated using the method as described by Lin.[111]

$$\% \text{ Conversion} = \frac{W_1 - W_0}{W_0} \times \frac{M_0}{M_1} \times 100 = \frac{W_1 - W_0}{W_0} \times 160.6$$

W_0 = wt. of polyacrylonitrile cloth before conversion

W_1 = wt. of polyacrylonitrile cloth after conversion

M_1 = molecular weight of hydroxylamine (33 gm/mole)

M_0 = molecular weight of acrylonitrile monomer unit (53 gm/mole)

From the results of the conversion of several batches of cloth presented in Table 1, several observations were made. The physical properties of the Orlon cloth, which was quite flexible and white in colour originally, changed markedly during the conversion process. Depending upon the degree of conversion to amidoxime groups, the cloth became increasingly less flexible, and it was observed that at higher degrees of conversion (> 50 %) the cloth also became brittle.

The colour of the cloth was observed to change from white to tan, to a light yellow in colour depending on the reaction conditions. The color change was originally attributed to the increase in the degree of conversion; however, later experiments indicated that the color change may also have been due to the prolonged heating of the cloth at temperatures greater than 60 °C, conditions which favour saponification.[129,130]

The choice of methanol as the solvent used with water seemed to produce a slightly better cloth than when ethanol was used. The cloth produced with methanol seemed to be more flexible and softer in texture. The use of NH_4OH as opposed to NaOH as the choice of neutralizing base produced no noticeable differences in the cloth.

The cloth was also observed to contract in size during the course of treatment, even enough to crack the glass frame supporting it. This effect is based on the physical nature of the thread and fibres which make up the thread. During manufacture, the fibres are produced by a hot extrusion process, which results in the manufacture of a fibre in an elongated form. The reason for this is that a high degree of order is introduced into the polyacrylonitrile chains during the extrusion process due to the high crystallinity that the polymer possesses.[129,130] The polymer is thus said to

be placed in a high energy metastable state. When subjected to a wet heating process the polymers relax to a lower energy state and thus the fibres will contract. This is the effect observed during the conversion process and the result is a contraction of the cloth.

Because of the two processes which occurred during conversion, the contraction of the cloth, as well as actual conversion of nitrile groups, the optimization experiments were performed. This was carried out in order to gain a better understanding of all of the processes which occurred during the conversion and to identify some of the variables involved regarding these processes. The eventual goal was the production of a cloth with good physical characteristics such as flexibility while having a high percentage of amidoxime groups. Another factor was that the production would be able to reproducibly manufacture cloth of similar characteristics in different batches in order to simplify calibration during the deployment of a large number of monitors.

3.1   CHARACTERIZATION BY FTIR SPECTROSCOPY

FTIR spectra were taken of some of the samples of cloth before and after varying degrees of conversion in order to qualitatively monitor the conversion process. Small selected pieces of cloth were cut into strips ~ 1 x 0.2 cm and placed in liquid nitrogen. After the cloth pieces were frozen they were ground into a powder with a mortar and pestle. The powder was combined with a small amount of KBr and a thin glass pellet was pressed. FTIR spectra were recorded from 600 - 4000 cm^{-1} at a resolution of 2 cm^{-1}. Representative spectra are presented in Figure 11. The use of an attenuated total reflectance cell to record spectra on the cloth was attempted without success.

Examination of the FTIR spectra recorded on three batches of converted cloth of differing degrees of conversion provides a qualitative and semi-quantitative account of the conversion process. The peak at ~ 2240 cm^{-1}, which corresponds to the nitrile group of the Orlon cloth, is seen to decrease as the degree of conversion increases, while at the same time the peak at 1600 cm^{-1}, which corresponds to C=N, broadens considerably. These results are similar to those reported by Lin.[111]

Figure 11. FTIR Spectra Recorded on Three Different Batches of Cloth.
Cloth used were batches 10 (upper), 15 (middle) and 17 (lower)
degrees of conversion = 17, 57 and 100 % respectively.
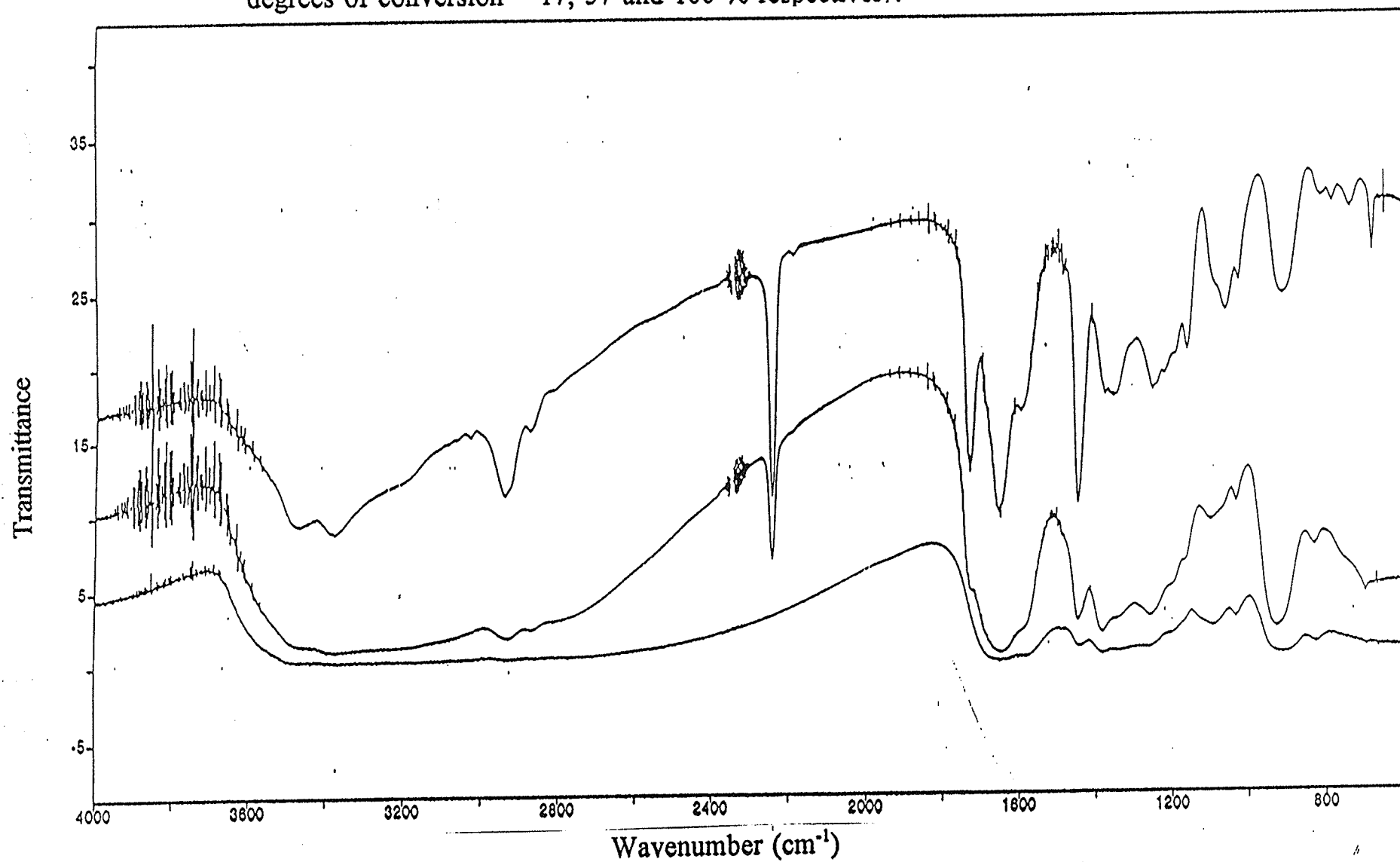
3.2 OPTIMIZATION OF REACTION CONDITIONS

A number of variables were investigated in an attempt to reproducibly manufacture cloth with good physical characteristics and a high degree of conversion of nitrile groups to amidoxime groups. Parameters investigated were the effects of initial pH, concentration of hydroxylamine, time of conversion and temperature of conversion. For these experiments small pieces of plain Orlon cloth were cut from the supplied material into squares ~ 6.13 cm^2 with the edges fused by a hot spatula. Conversion was carried out in 140 mL beakers containing 100 mL of the appropriate hydroxylamine solution.

3.2.1 EFFECT OF INITIAL pH

The effect of varying the initial pH of the hydroxylamine solution on the degree of conversion was investigated. Hydroxylamine solutions of pH = 2 - 10 were prepared via addition of dilute HCl or NH_4OH to a stock solution of 2 % (w/v) of hydroxylamine in 50 % (v/v) ethanol(95%)/ water. Conversion was carried out in 100 mL each of the solutions for 63.25 hours at 50 °C followed by 9.75 hours at 60 °C.

From the results regarding the effect of the initial pH on the degree of conversion as shown in Figure 12, it was observed that at a pH of 7 the highest degree of conversion was obtained. This was presumed to be due to the mechanism of the reaction being an S_N2 type of reaction, with the hydroxylamine attacking the nitrile carbon, which is preferentially favoured at a neutral pH. Thus a pH of 7 was chosen for the conversion of the cloth. This is similar to results obtained for the conversion of polyacrylonitrile staple fibres.[111]

3.2.2 HYDROXYLAMINE CONCENTRATION

The effect of the initial concentration of hydroxylamine on the degree of conversion and the physical properties of the cloth were investigated. The initial concentration of hydroxylamine was varied between approximately 1 and 7 weight % in 100 mL of solution via serial dilution of a freshly prepared 1 Litre stock solution of hydroxylamine 3 % (w/v) in 50 % (v/v) ethanol/ water. Conversion was carried out in 100 mL solutions each of differing concentrations for 1.5 hours at 80 °C.

Figure 12. Effect of pH on the Degree of Conversion
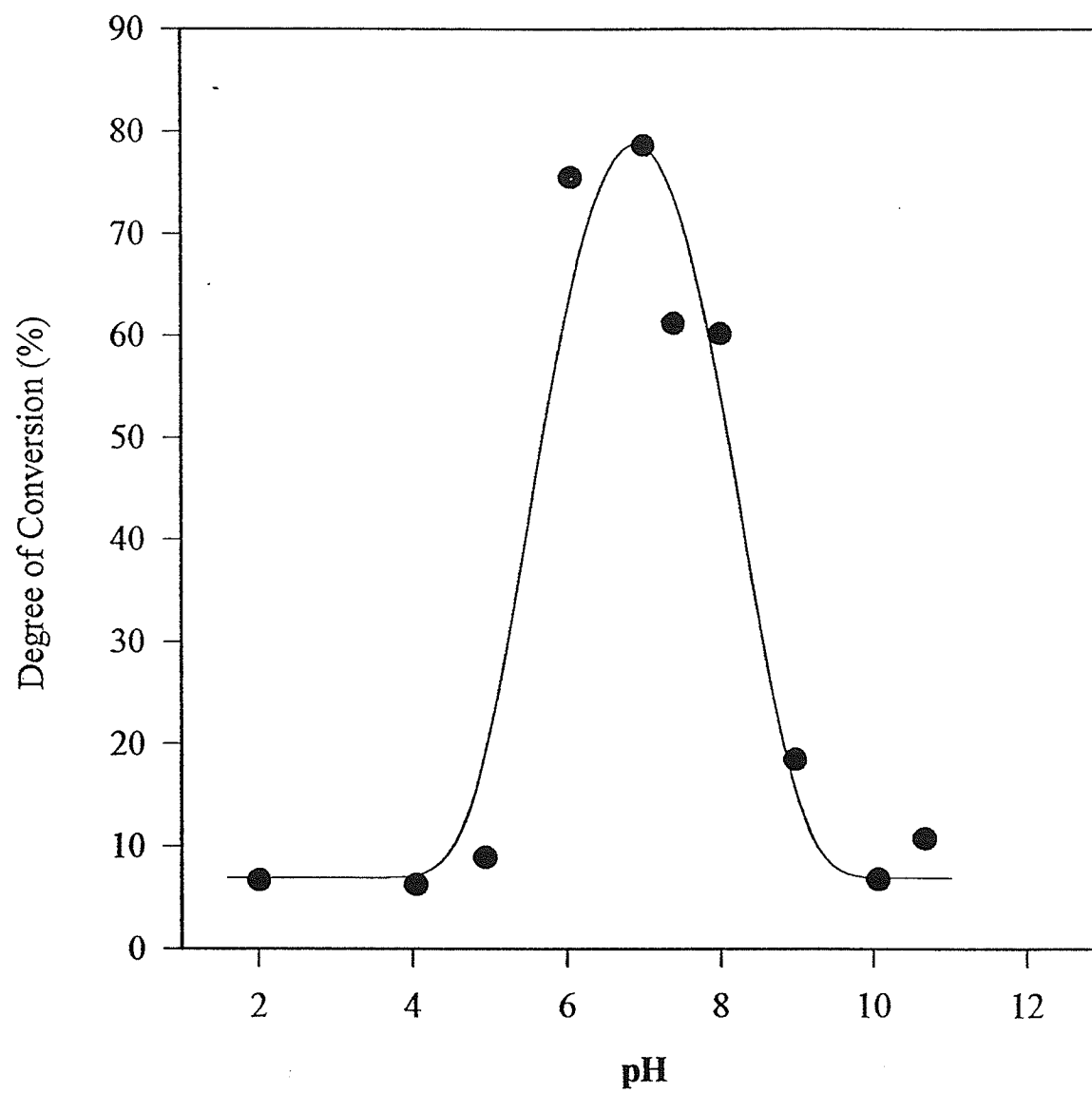
Several observations were made with respect to the effect of the initial concentration of $NH_2OH*HCl$ on the degree of conversion as can be seen in Figure 13. It was observed that the degree of conversion initially was relatively slow up to a concentration of ~ 3.5 % (w/v) after which the conversion increased substantially, reaching a plateau at > 6 % (w/v). The slow initial rate was presumed to be due to the diffusion of NH_2OH through solution being rate limiting. After the steep rise, the surface reaction was presumed to be the rate limiting step. These results are similar to the results observed on the conversion of polyacrylonitrile staple fibres.[108-111]

Another interesting fact was that the degree of conversion was observed to be greater than 100 % for cloth produced at concentrations of $NH_2OH*HCl$ greater than ~ 4.5 % (w/v). The cloth produced at these higher concentrations was also observed to be smooth and brittle compared to the cloth produced at lower concentrations of $NH_2OH*HCl$. This higher than theoretically possible degree of conversion may be attributed to the formation of ring and ladder structures as shown in Figure 14. The result is the linking the amidoxime groups on the surface of the cloth, something that has been observed with the conversion of fibres.[100,123] A side effect of this process is the production of a cloth that is unsuitable for use in the monitors.

Figure 13. Effect of $NH_2OH*HCl$ Concentration on the Degree of Conversion
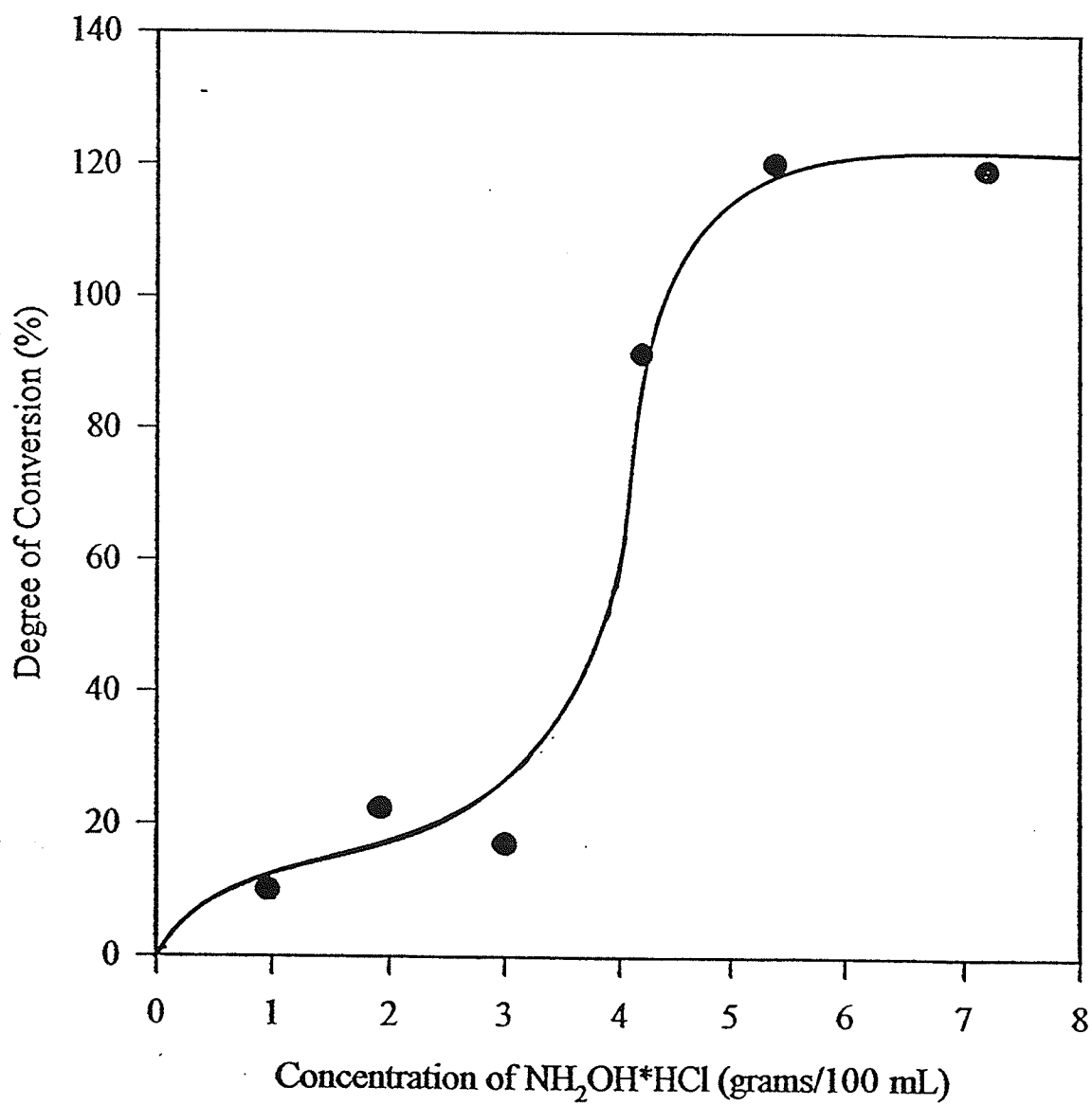
Figure 14. Diagram of Several Possible Secondary Structures Which May Form from the Polyacrylamidoxime Precursor.[100, 123]

Polyacryloamidoxime

Imidedioxime   **Imidemonoxime**

Ring Structures

Ladder Structure

Amide   **Carboxylic Acid**   **Hydroxamic Acid**
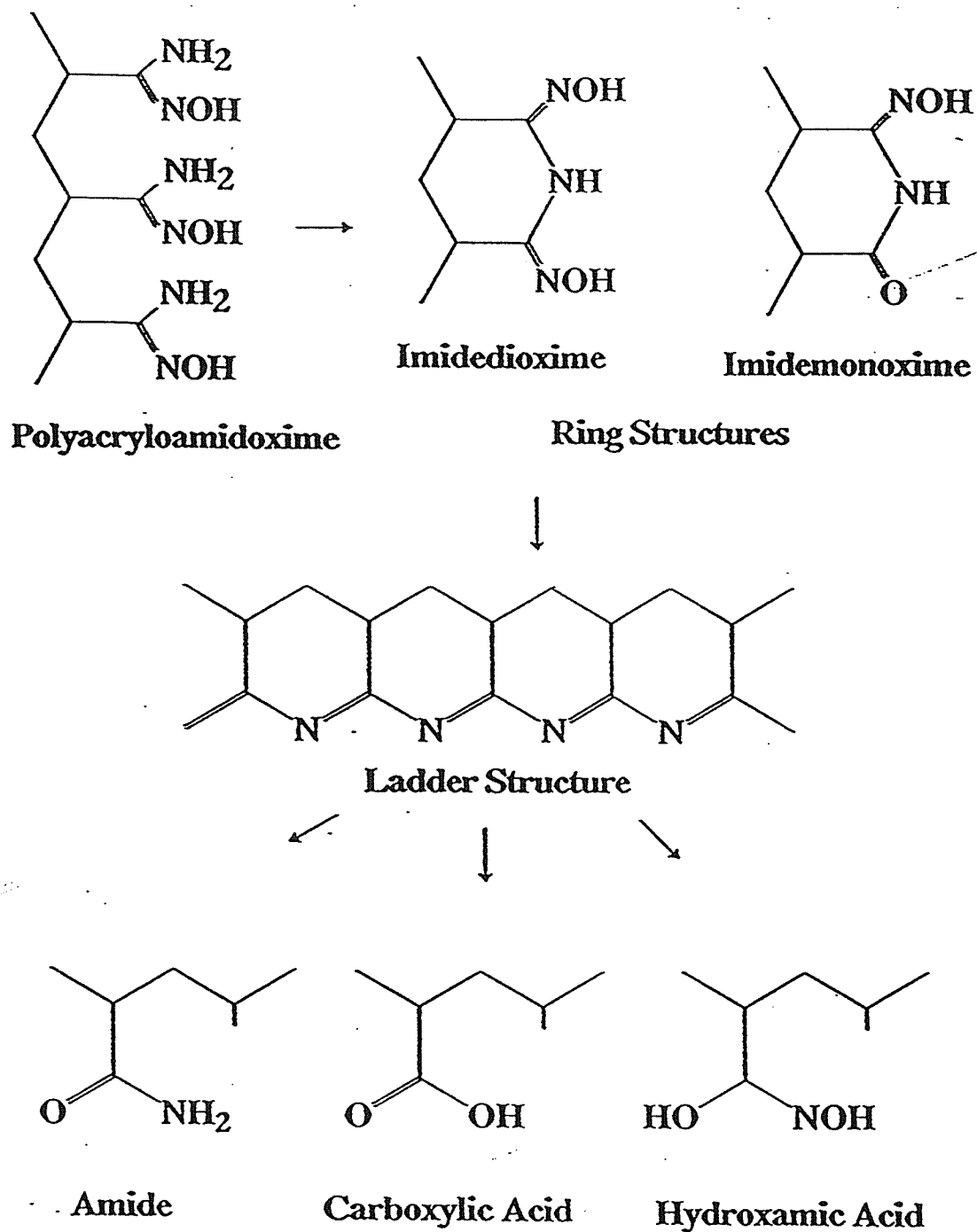
It is noted that this effect was also observed with the production of the cloth in batch # 32 in which the hydroxylamine solution used previously was recycled along with the addition of 60 grams of $NH_2OH*HCl$. This resulted in the concentration of NH_2OH in solution being much greater than anticipated, ~ 1.85 times. The cloth produced was brittle and possessed a smooth surface.

Because the production of the secondary structures was undesirable, a concentration of $NH_2OH*HCl$ of 2 % (w/v) was deemed optimum for the reproducible production of cloth with the desired properties. At this concentration the conversion process was slower and thus deemed more controllable.

3.2.3 TIME AND TEMPERATURE EFFECTS

Both the time of conversion and the temperature of conversion were investigated as to their effect on the degree of conversion and the physical properties of the cloth. The conversion of the cloth was carried out at different temperatures (35, 52, 60, 75, and 80 °C) over different time intervals of up to 5 days, in order to observe the effect of each variation, and to try and optimize the manufacturing procedure. Initially, 100 mL

hydroxylamine solutions were used to treat small pieces of cloth. The conversion was carried out by heating the solutions on hot plates without stirring. Results are shown in Figure 15. The rate of conversion was calculated from the linear slope of each of the curves derived for the different temperatures. The results are shown in Figure 16.

The effect of reaction time was later investigated with larger pieces of cloth using the circulating water bath vertical tank reactor. The concentration of $NH_2OH*HCl$ was 2 % (w/v) in ~ 3 Litres of 50 % methanol/water (v/v). Conversion was carried out for varying lengths of time (up to 24 hours) with a constant temperature of 55 - 56 °C. Results are shown in Figure 17.

It can be seen in Figure 15 that, as the temperature of the reaction was increased, the degree of conversion increased linearly with the exception of the results at 60 °C. The change in the slope at 60 °C was presumed to be due to a slow initial hydration process of the cloth which is relatively hydrophobic, followed by the more rapid reaction with hydroxylamine. The degree of conversion at the low temperatures was observed to be exceedingly slow while at the higher temperatures the rate was too fast and the cloth produced was brittle. The cloth produced at 60 °C seemed to be the best

Figure 15. Temperature Effect on the Degree of Conversion
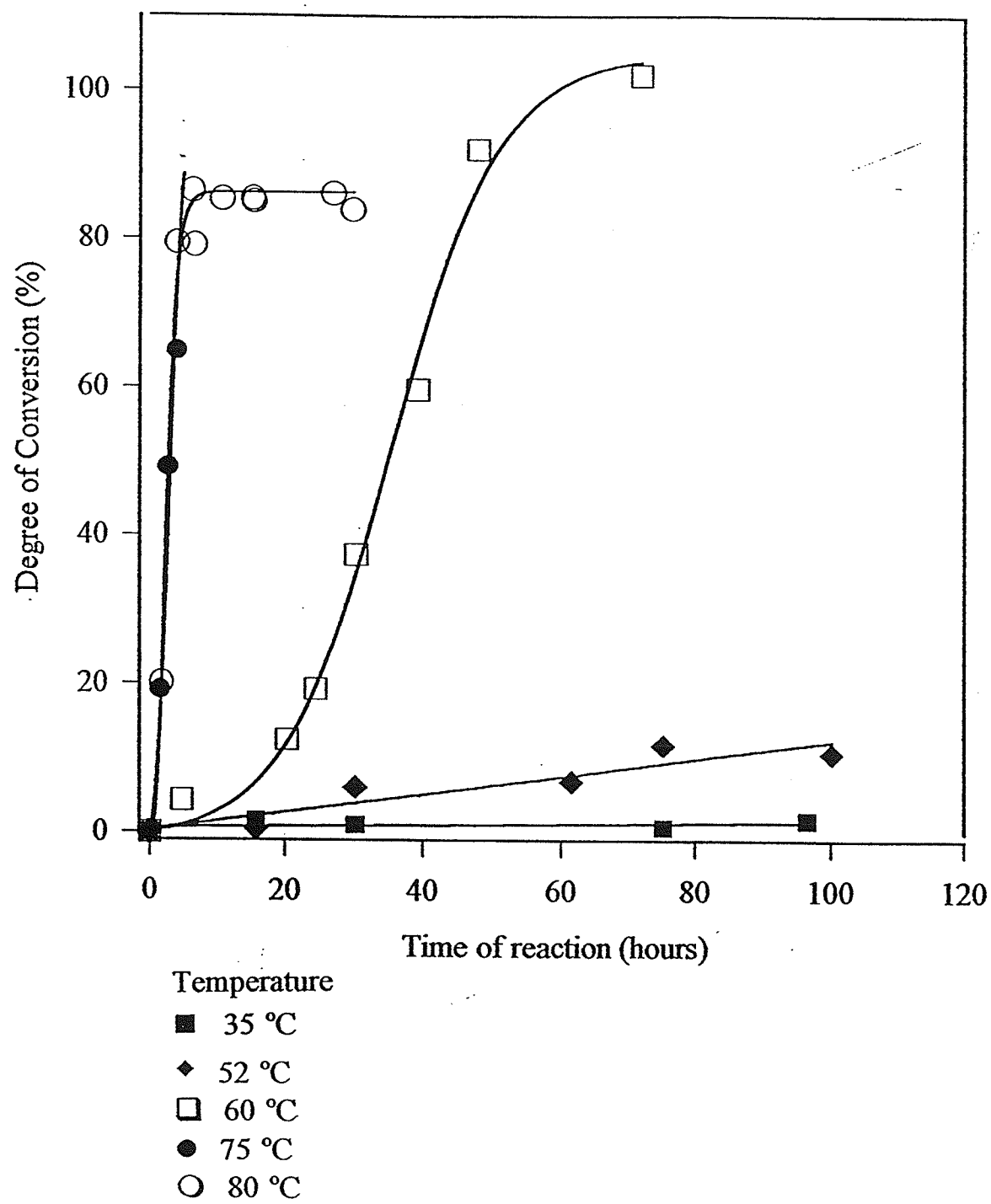
Figure 16. Observed Rate of Conversion at Different Temperatures
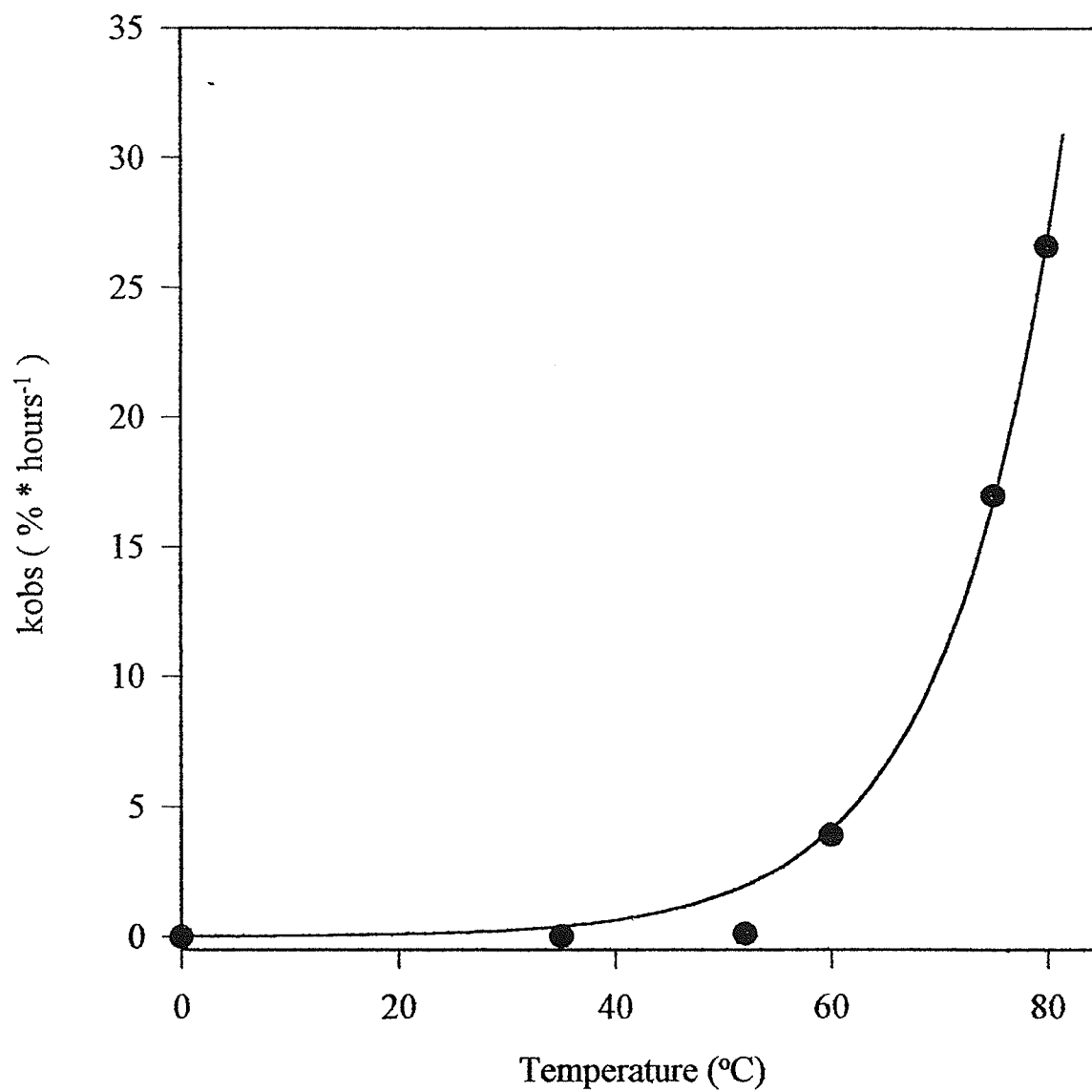
Figure 17. Effect of Time of Reaction on the Degree of Conversion at 55 °C
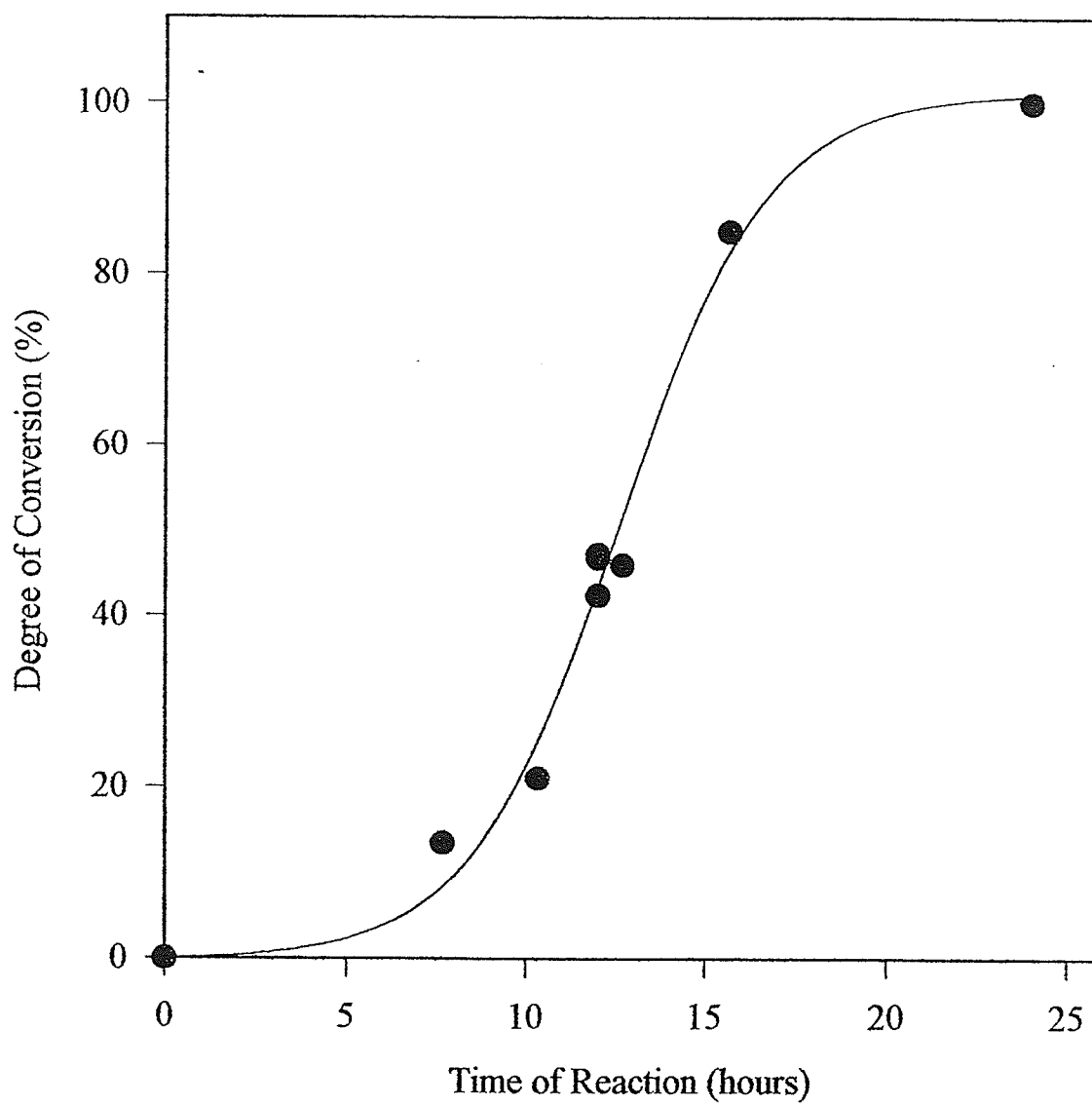
compromise between speed of conversion and quality of the cloth produced.

From previous research, it was observed that at higher degrees of conversion (> 50 %) the cloth actually became less receptive to the uptake of metal ions from solution as well as becoming more brittle, something that was confirmed here.[81,127] It was thought that, as the degree of conversion is increased, a side reaction involving the fusing of the cloth fibres took place thus decreasing both the nominal surface area of the cloth and resulting in the cloth's brittleness. This then resulted in a decrease in the effective chelating surface area of the cloth and a subsequent reduction in the uptake of metals. Evidence to support this is found in the differences in the maximum degree of conversion as measured at 65 °C and 80 °C from the results presented in Figure 15. It can be seen that at 65 °C the conversion process is relatively slow, which allows the entire bulk of the textile to react with hydroxylamine resulting in a degree of conversion approaching 100 %. However, at 80 °C, the upper limit of conversion approached only ~ 85 %. The reason for this is twofold, the first of which is contraction of the cloth due to the thermal shrinkage. The second cause is due to the fusing of the cloth fibres on the surface of the textile as evident in the smoothness of the surface of the cloth after the conversion process at these higher temperatures.

This fusing results in decreasing the net effective surface area that may react with the hydroxylamine and thus decreases the degree of conversion.

The observed rate of conversion was calculated from the linear slopes of each of the curves for the different temperatures used. From the results in Figure 16 it was observed that the rate of conversion was slow initially up to a temperature of about 60 °C after which the rate increased rapidly. Because it was deemed necessary to prepare the cloth as reproducibly as possible, the lower temperatures of conversion were chosen. The other criteria for the conversion of the cloth was that the conversion process should not be too long. For these reasons a temperature of 55 °C was chosen as being optimum as this allowed more control in the manufacture of different batches of cloth with the same degree of conversion while possessing good physical properties.

The results of the optimization experiments were extended to the larger scale batch preparation processes of the chelating cloth. The temperature of 55 °C was used and the results are shown in Figure 17. From these results it is clear that the processes involved with the smaller scale conversion experiments are the same as those of the larger scale experiments. As the time of conversion at 55 °C was increased so did the degree of conversion

up to a point past ~ 50 % where the cloth became less flexible and more brittle. From these results an optimum time of conversion of 12 hours was chosen. The 12 hour time interval was also chosen for convenience.

3.3   SUMMARY

The net result of the research into the parameters involved with the preparation of the chelating cloth was the production of a material suitable for the production of passive monitors. The cloth prepared was flexible and had a relatively high degree of conversion. The cloth was able to be reproduced in successive batches with a reasonable degree of reliability. The optimized parameters chosen are summarized in Table 2 and the properties of the final selected batches of cloth are summarized in Table 3.

Table 2. Optimized Reaction Conditions

Parameter Optimized	
Time of Conversion	12 hours
Temperature	55 °C
$NH_2OH*HCl$	2.0 grams 100 mL^{-1} (2 % w/v)
Solvent	50 % (v/v), Methanol/ H_2O
Optimized pH	pH = 7

Table 3. Cloth Produced Given the Optimized Reaction Conditions

Properties	
Degree of conversion	45 % +/- 2 %
Color	White
Physical properties	Flexible and soft
Total surface area density	0.043 grams /cm^2
Amount of amidoxime group	206 mmol /cm^2
Size of monitor	8.05 cm^2 (one side)

CONTROLLED LABORATORY EXPERIMENTS

4   INTRODUCTION

In order to test the physical properties of the cloth with respect to the sorption of different metals from solution, a series of both batch and flow experiments were used. The correlation between the cloth and previous work with fibres and resins was also investigated in order to determine if the physical properties of cloth mimic those of the fibre and/or the macroporous resin. Amidoxime-containing cloth, with varying degrees of conversion as prepared in the preceding section, were used for all experiments. As it was not practical to conduct these experiments with a large number of metals, only two were used for the bulk of this work. The two metals, Pb(II) and Cu(II), were chosen for two different reasons, Pb(II) because of its environmental significance and Cu(II) because it is the metal of choice for the study of the chelating properties of resins, etc. In addition, Pb(II) and Cu(II) bind with different degrees of stability to amidoxime resins, with Cu(II) >> Pb(II) in stability, and thus should provide a representation of all the metals which chelate with the amidoxime group.[83,122]

In order to evaluate the ability of the cloth to act as a passive monitor, a number of *in vitro* tests were performed with a flow chamber designed to simulate the sampling environment. Monitors or pieces of cloth were attached to a glass frame with cotton thread and exposed to the solution passing through one of the flow chambers described earlier. The variables investigated with respect to the rate and amount of sorption of metals were: the time of exposure, the amount of amidoxime groups on the surface of the cloth, the flow rate of solution, the degree of precision which could be expected, the use of TiO_2 as an internal standard, the rate of desorption of metals from the cloth, and the effect of conditioning the cloth with HCl on the rate of metal uptake.

A series of batch experiments were carried out in order to further examine the physical properties of the cloth. Experiments were performed on small pieces of cloth placed in 250 mL conical flasks. The flasks were placed on very low speed on a shaker to ensure that the cloth pieces did not adhere to the sides of the flask. The variables investigated were the effect of initial concentration of the metal in solution, the effect of temperature on the rate of sorption for Pb(II), the effect of site competition, or inhibition, between Cu(II) and Pb(II), the use of chelate-bound Au(III) as an internal

standard, and the effect of conditioning the cloth with NaOH or NH_4OH. As well, an attempt was made to measure the capacities of the cloth for Cu(II) and Pb(II).

4.1 KINETICS OF METAL UPTAKE

The effect of the length of time of deployment on the amount of metal taken up by the monitors exposed to a constant flowing stream containing trace amounts of Pb(II) and Cu(II) was investigated. The flow chamber in Figure 2 was used, with the flow rate of solution fixed at ~ 4.7 Litres/ minute, with a linear velocity of ~ 52 cm/ minute. The initial concentrations of Pb and Cu in the barrel/ flow chamber were determined with GFAA to be 3.5 and 4.8 µg/Litre (0.017, and 0.075 µmol/L) respectively in ~ 190 litres.

Monitors were prepared (cloth batch # 6, 7 % conversion), attached to glass racks and placed in the flow chamber for times ranging from 7, 17, 21, 24, 31, to 44 days. After exposure, they were removed from the chamber and dried in air. Analysis of the amounts of metals sorbed during exposure was done with EDXRF using a spectral acquisition time of 3000 seconds.

A spectrum showing the peaks due to the sorption of Pb and Cu from the flow chamber is presented in Figure 18. The peaks of interest are: Ti, Cu and Pb at ~ 120, 300, and 440 channel numbers respectively. It was observed that a substantial amount of noise was present in the baseline of all spectra recorded. This unavoidably led to a large relative error in the peak integration of the spectra.

The results showing the dependence of the amount of Pb and Cu sorbed on the cloth with respect to the time of exposure are presented in Figures 19 and 20. The curves presented were derived from the best fit parameters used in Table Curve. The amount of Pb and Cu sorbed were represented in the form of the equilibrium distribution coefficient Kd.[116,131]

$$K_d = \frac{(\mu mol\ metal/\ gram\ cloth)}{(\mu mol\ metal/\ mL\ solution)}$$

It is noted that this measure provided only an estimate of Kd, as equilibrium had not yet been reached, as indicated by the upwards slope of the graph. These results also provide a measure of the degree of sample preconcentration from solution and at the same time normalize the results with respect to the initial concentration of metals in solution.

Figure 18. EDXRF Spectra recorded on one of the Monitors Before (lower) and After Deployment (upper) in the Flow Chamber. Peaks correspond to Ti, Cu and Pb at 120, 300 and 440 channel numbers respectively.
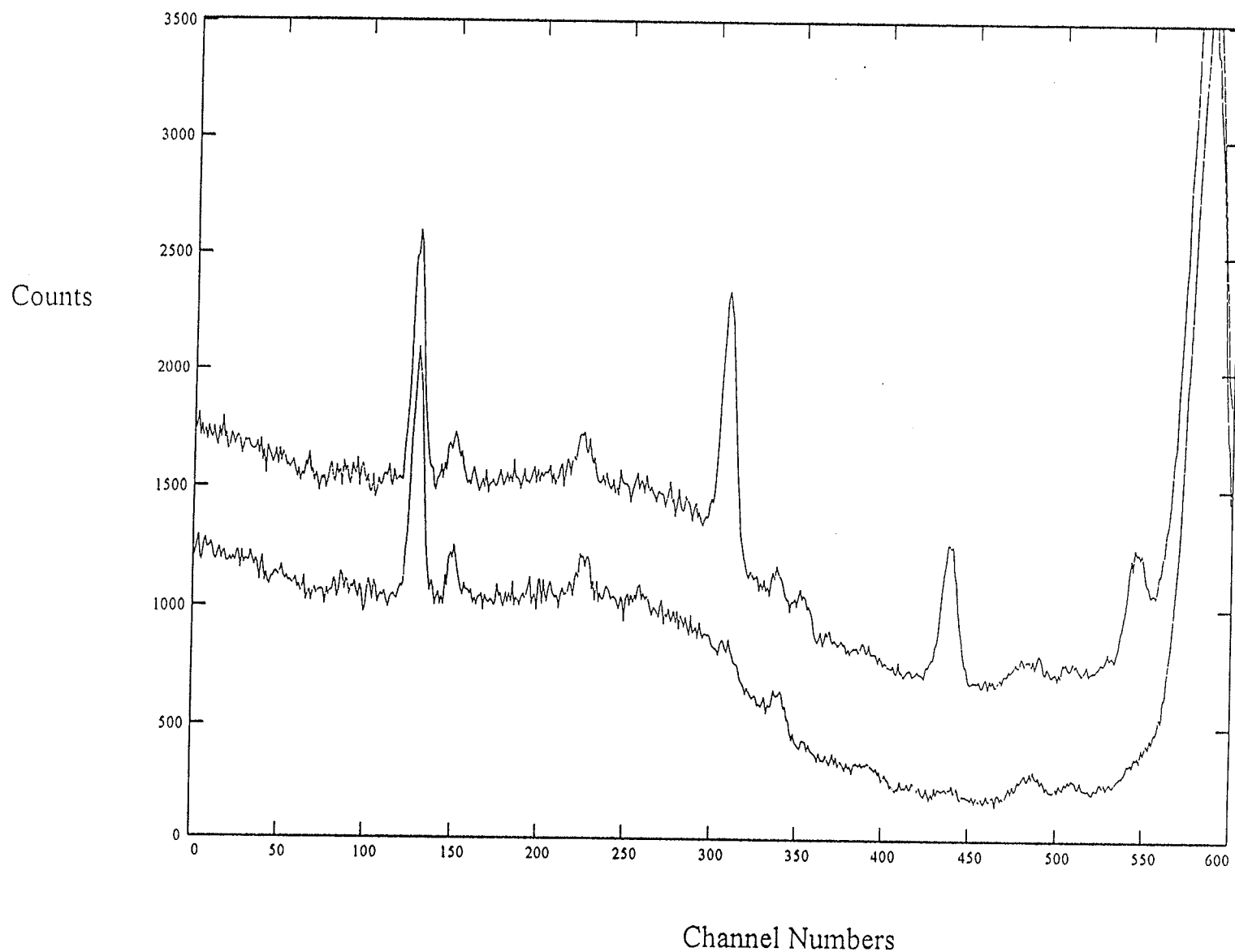
Figure 19. Rate of Sorption for Pb(II)
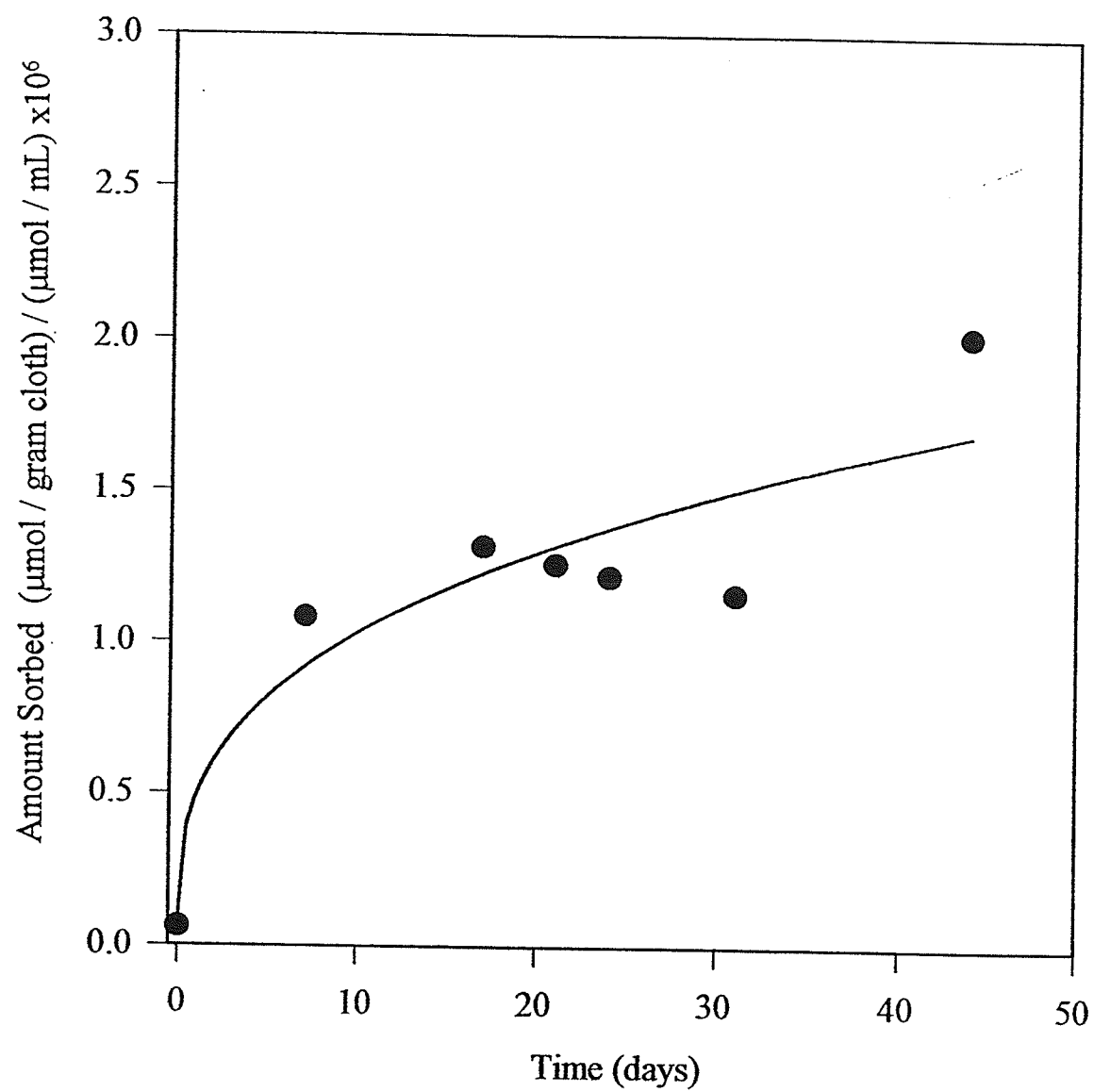
Figure 20. Rate of Sorption for Cu(II)
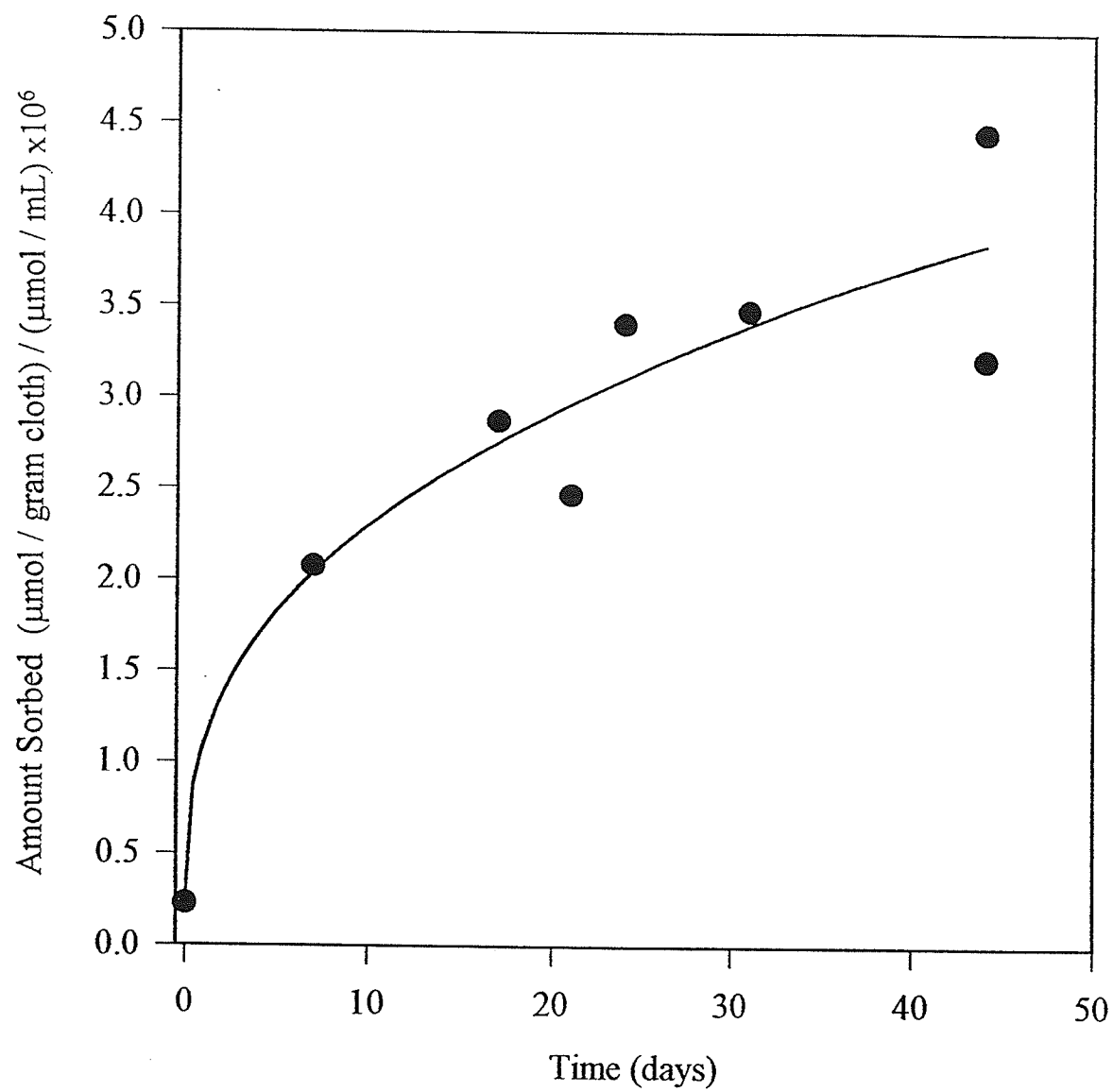
The general shapes of the curves in Figures 19 and 20 indicate that the rate of uptake of Cu and Pb were initially quite rapid. After this the rate is observed to decrease somewhat but does not appear to approach a limiting value. The kinetic profile observed was similar to the general shape of results reported by others with respect to the rates of metal uptake by chelating polymers such as resins[89-91,118,119] and fibres.[97,104,105,108,109] Closer examination of the shapes of the curves which were fit to the data suggest that the initial rates appear to be similar. At this time, this cannot be proven due to the lack of initial data points.

The rate of metal uptake was calculated from an averaged daily value for the duration of exposure. The values were 600 μg/gram/day (9.4 μmol/gram/day) for Cu and 200 μg/gram/day (0.96 μmol/gram/day) for Pb, values in the same range as those observed for the sorption of $UO_2(VI)$ of 200 μg/gram/day (0.84 μmol/gram/day) from seawater.[115] The rates of uptake normalized to the average concentration of metal in solution were 100 (μmol/gram/day)/(μmol/L) for Cu and 71 (μmol/gram/day)/(μmol/L) for Pb. The total amount of Cu sorbed was observed to be much greater than Pb, even after only a few days of exposure. The value at 30 days Kd = $3.5*10^6$ for Cu was approximately double that of the value Kd = $1.5*10^6$ for

Pb, values which are in agreement with those observed for the sorption of UO$_2$(VI).[116,122] The value K_d Cu was greater than K_d Pb because Cu(II) forms a much stronger chelate complex with amidoxime than Pb(II).[83,122,123] Another contributing factor was that during the experiment, the concentration of Pb in solution was observed to decrease slightly from 0.017 μmol/L to 0.010 μmol/L after 44 days, whereas the concentration of Cu in solution was observed to increase slightly from 0.075 μmol/L to 0.11 μmol/L. The decrease in the Pb concentration was thought to be due to sorption by the cloth while the increase in Cu in solution was thought to be due to leaching of Cu from the material the barrel was made of, a blue coloured polymer (blue Cu salts are used as colouring agents) or from materials used in the manufacture of the submersible pump. These changes during the course of the experiment may account for the small variation in the shape of the Cu and Pb curves.

It was observed that there was a great deal of variability in the results. One source of variation was attributed to the cloth used for each sampler, specifically, differences in the tightness of the weave of the cloth which was introduced during the manufacturing process. This variation would have resulted in slightly different effective surface areas for chelation of the

metals by the cloth. There was also a relatively large amount of noise present in the spectra which resulted in a relatively large error during spectral analysis.

Another source of variation was due to a noticeable amount of turbulent flow present within the flow chamber. As the samplers were exposed at different locations within the flow chamber they would experience different degrees of turbulence. This difference would affect the results substantially as the rate limiting step of metal uptake was presumed to be diffusion.

4.2   DEGREE OF PRECISION

An experiment was performed with the flow chamber in order to investigate the relative error involved in sampling under the near ideal conditions present in the laboratory. A total of 15 monitors were prepared (batch # 5, ~ 30 % conversion). They were then placed in the flow chamber used previously for times of 4, 7, 11 and 15 days. The initial concentrations of Pb and Cu as determined with GFAA were 2.0 and 6.9 μg/Litre (0.010 and 0.11 μmol/L) respectively in ~ 190 litres.

The monitors were removed in groups of three from random positions in the flow chamber during the course of exposure with the exception of the last set which consisted of a group of six monitors. After the monitors were dry, analysis of the amounts of metals sorbed during exposure was done with EDXRF, again with a spectral acquisition time of 3000 seconds.

The results indicating the precision of the monitoring with respect to the time of exposure are presented in Table 4. Initially there was a relatively large error present which decreased as the length of exposure, and the size of the peak, increased. The source of variation was attributed to the presence of turbulence in the chamber and the noise present in the spectra. After the initial period of time the surface of the cloth becomes more or less saturated and less influenced by a change in the flow rate. There was also less error introduced during the analysis of the larger peaks recorded on the later samples. The best result observed was for Pb at 15 days in which the relative standard deviation was only ~ 6 %, a value which would be quite acceptable for environmental applications.[93]

Table 4. Degree of Precision in Replicate Measurements

time of exposure	EDXRF mean peak area (error)		% error	
(days)	Cu	Pb	Cu	Pb
4	2400 (500)	2700 (310)	20	12
7	2600 (540)	3200 (250)	20	8
11	2700 (190)	3000 (200)	7	7
15	3100 (300)	3500 (220)	9	6

4.3   KINETICS OF METAL UPTAKE / DEGREE OF CONVERSION

An experiment was performed in order to investigate the effect of the amount of amidoxime groups present on the surface of the cloth versus the amount of Pb(II) and Cu(II) taken up by the cloth. Monitors were prepared with cloth of different degrees of conversion to amidoxime groups (batches # 2, 6, 7, 5 and 3; 7, 7, 22, 28 and 50 % conversion respectively). They were then exposed for varying lengths of time, of 7, 17 and 24 days, to the flow chamber under the same conditions as described in section 4.1. Analysis of the amounts of metals sorbed during exposure was done with EDXRF using a spectral acquisition time of 3000 seconds.

The results showing the dependence of the amount of Pb(II) and Cu(II) sorbed with respect to the time of exposure using cloth of increasing degrees of conversion are shown in Figures 21 and 22. The general shapes of the curves are similar to those observed earlier in this work as well as work by others.[89-91,104,105,108,118,119]   The amount of Pb sorbed was observed to increase with an increasing degree of conversion, whereas the amount of Cu sorbed appeared to be independent of the degree of conversion with the exception of the results at 24 days.

Figure 21. Amount of Pb Sorbed on Cloth of Increasing % Conversion

Degree of Conversion
- □　7 %
- ○　22 %
- ◆　28 %
- ●　50 %
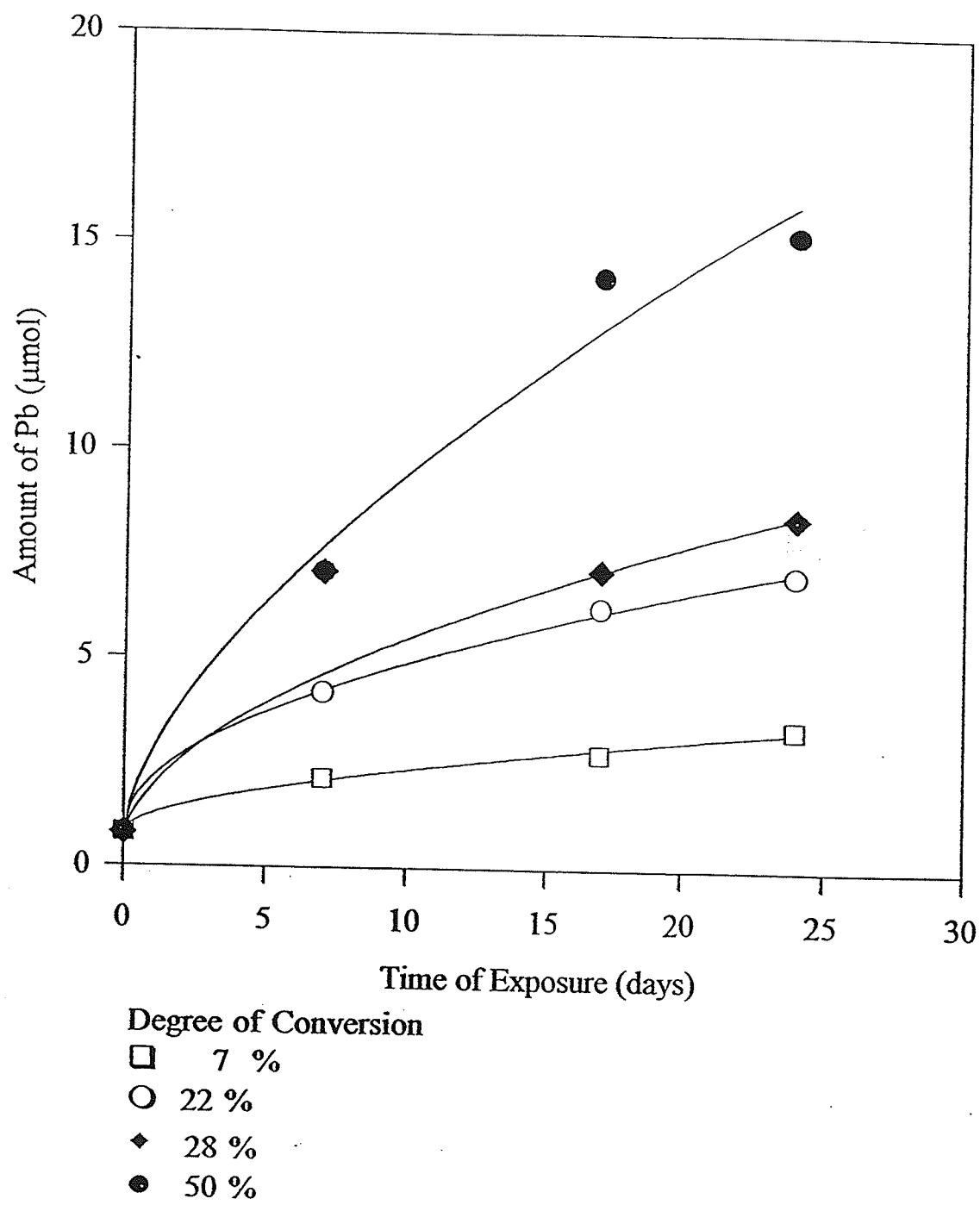
Figure 22. Amount of Cu Sorbed on Cloth of Increasing % Conversion
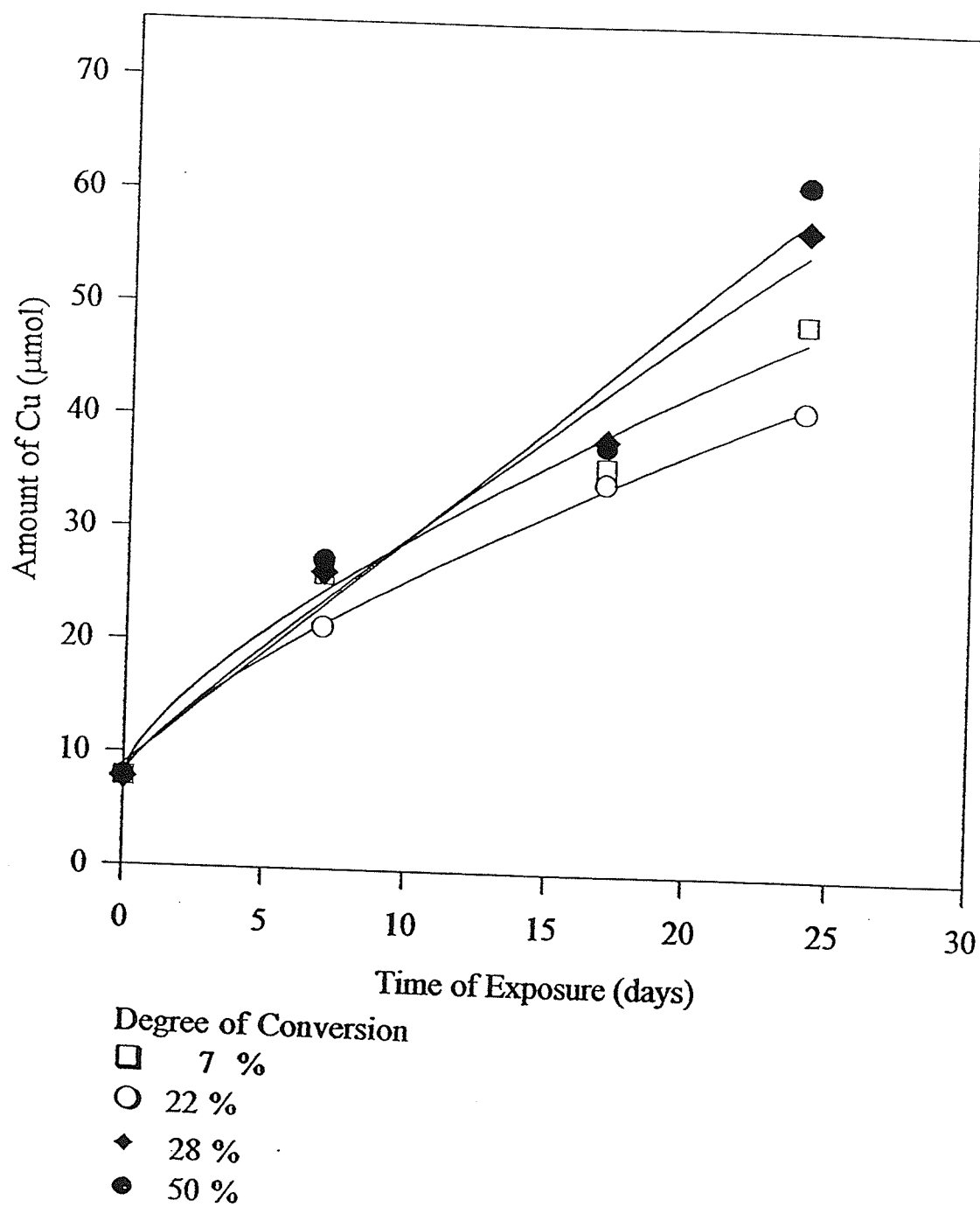
In the case of the Pb results, the shape of the curve is representative of the process of sorption where a weak complex is formed and the rate of sorption is similar to the rate of desorption, whereas the Cu results are indicative of the formation of a strong complex where the rate of sorption is much larger than the rate of desorption.[132]

The results showing the dependence of the amount of Pb(II) sorbed with respect to the degree of conversion are given in Figure 23. It was observed that the relationship between the amount of Pb sorbed and the degree of conversion was linear, a phenomenon observed with heterogeneous kinetics where adsorption is the rate limiting step.[132] The results for the uptake of Cu with respect to the degree of conversion, as shown in Figure 24, were observed to be somewhat different. It appears that, for each increasing degree of conversion, Cu reaches a limiting value with respect to the amount sorbed by the cloth, a phenomenon which is observed in heterogeneous kinetics in which a strong complex is formed and the formation of the complex is rate limiting.[132]

The explanation for the differences in the observed Pb and Cu sorption curves is based on two facts. The first is that, during the conversion process, the outer portion of the cloth may be considered to be fully converted to

Figure 23. Effect of the Degree of Conversion on the Sorption of Pb(II)

Degree of Conversion (%)

Time of Exposure
- ☐ 7 days
- ○ 17 days
- ● 24 days
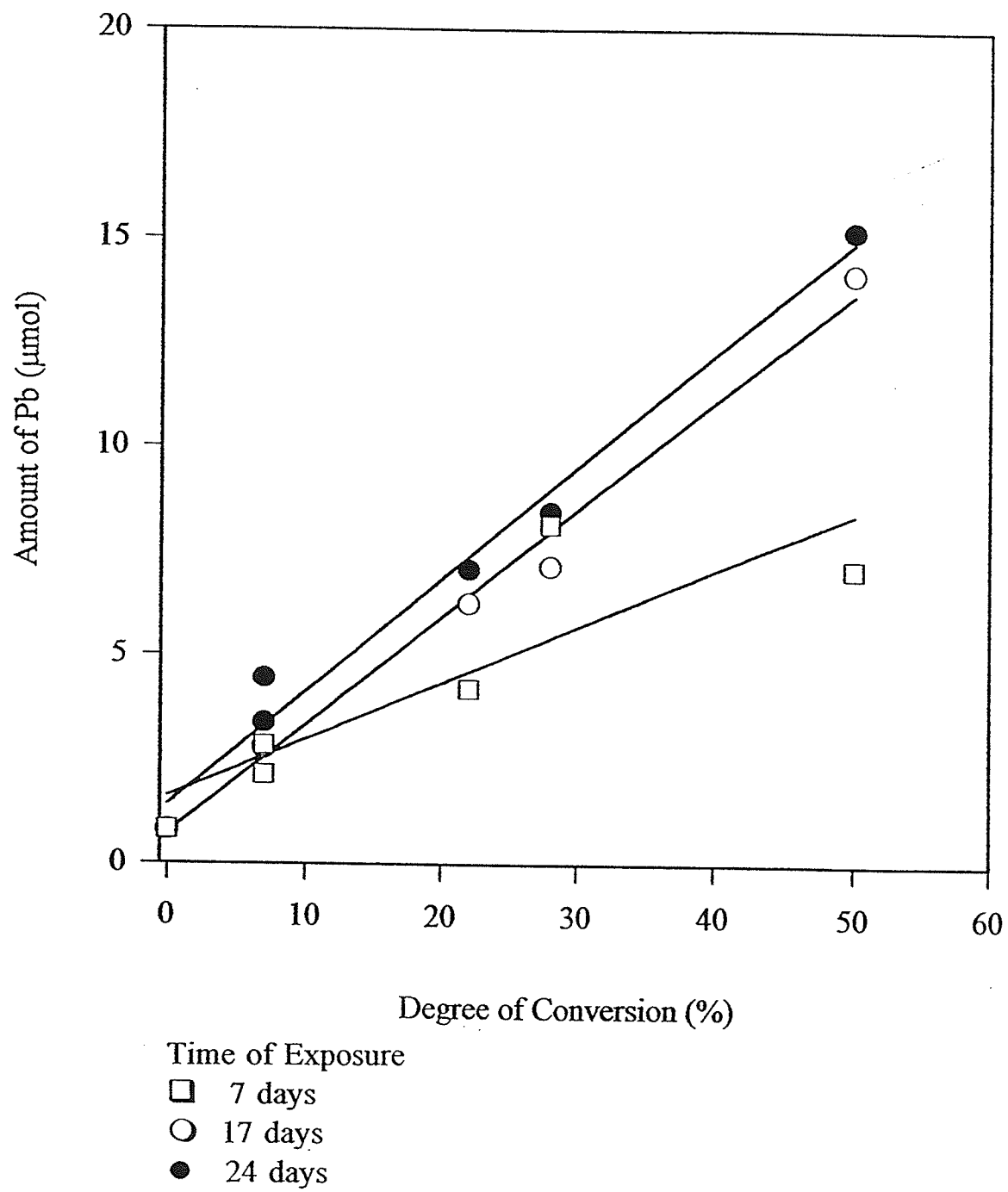
Figure 24. Effect of the Degree of Conversion on the Sorption of Cu(II)

Degree of Conversion (%)

Time of Exposure
□ 7 days
○ 17 days
● 24 days
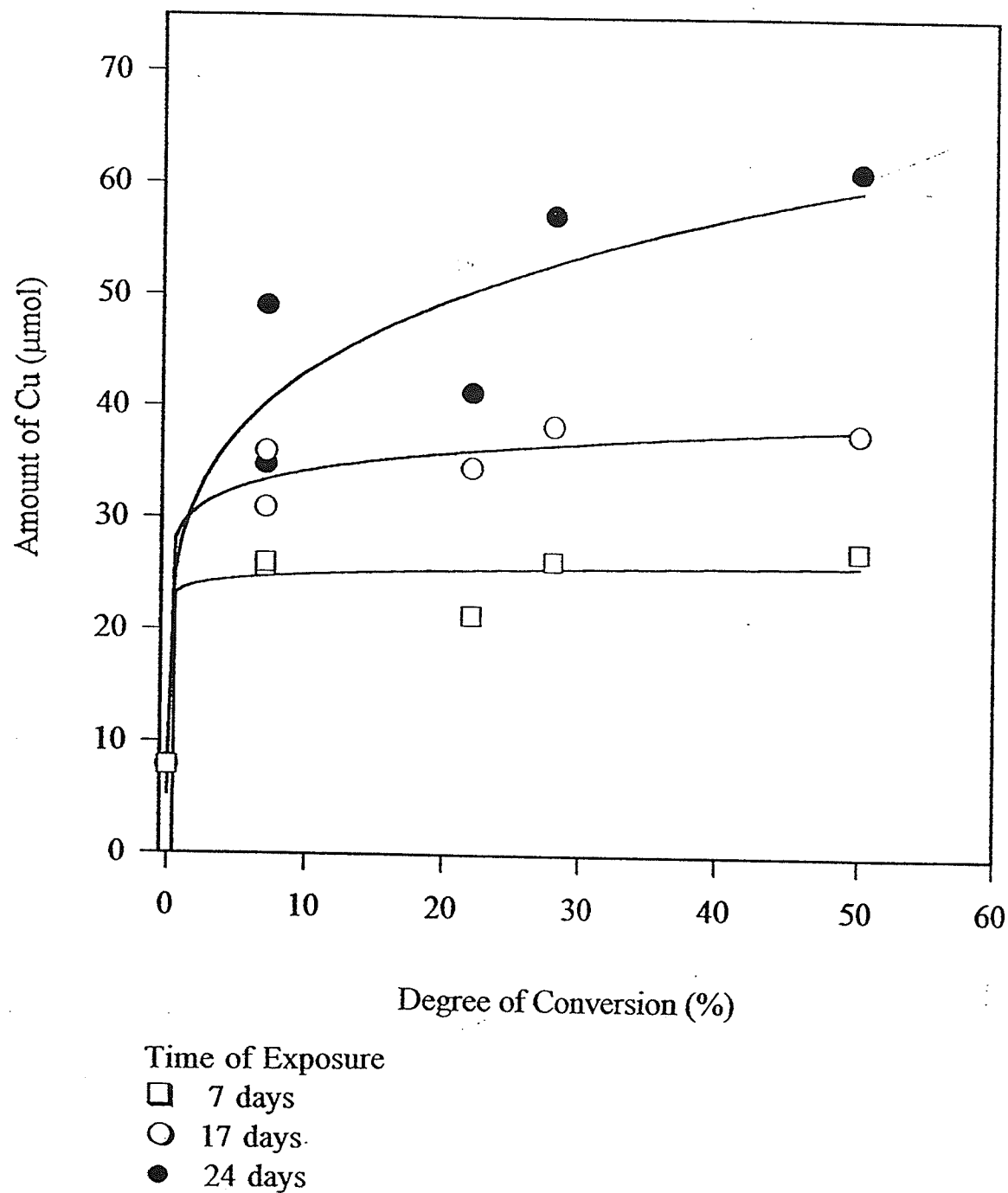
amidoxime chelating groups. Thus, after a given degree of conversion, for example 10%, the surface of the cloth had been fully converted to amidoxime groups and any subsequent conversion took place with the nitrile groups towards the centre of the cloth.

The second reason is due to the relative stabilities of the complexes formed by Pb(II) and Cu(II) with the amidoxime group and hence the resulting kinetics involved. It is known that Pb(II) prefers the formation of a complex with a single amidoxime group, (K_d Pb > K_d Cu); whereas Cu(II) preferentially forms complexes with two or three amidoxime groups, (K_d Cu > K_d Pb).[122] The result is that the overall stability of the Pb-(amidoxime) complex is much less than that of the Cu-(amidoxime)$_2$ complex due to the increased stability of the latter from the chelation with the second amidoxime ligand.

The sorption of Cu and Pb from solution may be expected to involve first, the saturation of the more readily accessible sites on the outer surface of the cloth, followed by interaction with sites within the interior. The rate of migration of ions to the interior of the cloth will depend on the rates of adsorption and desorption from exterior surface sites as well as the rate of diffusion into the interior from the bulk solution.

In the case of Pb, where a weak complex is formed relative to the Cu-amidoxime complex, assuming a similar rate of sorption, the rate of desorption will be much larger. Thus, the surface-complexed Pb is able to desorb and migrate at a relatively fast rate towards the interior of the cloth compared to Cu. This is confirmed in Figure 23 where it is shown that the amount of Pb sorbed is linearly dependent on the increasing degree of conversion of the amidoxime groups.

In the case of Cu, assuming a similar rate of sorption, the rate of desorption will be much smaller due to the strength of the Cu-(amidoxime)$_2$ complex compared to that of the Pb-amidoxime complex. Because of this behaviour, Cu will not desorb to the same extent and will migrate at a much slower rate towards the centre of the cloth only after surface saturation. This corresponds to the limiting values of the curves observed in Figure 24 where the initial Cu sorbed may be expected to be found only on the surface of the cloth which is essentially saturated with amidoxime groups. The curves obtained for 17 and 21 days suggest a slow rate of migration into the interior of the cloth after the initial surface saturation.

4.4 FLOW RATE

The effect of a variation in the flow rate on the resulting uptake of metals from solution was investigated because of the effect of the turbulence observed in previous experiments, and the fact that the flow of water in the environment is expected to vary considerably. In order to simulate different flow rates in the laboratory while keeping all other variables constant, a flow chamber apparatus was used which allowed for the simultaneous measurement of 5 different flow rates when used in conjunction with the original flow chamber/ barrel. A diagram is shown in Figure 3. It is noted that there was essentially no turbulence in this set of flow chambers, and that the flow involved could be considered nearly laminar.

A total of 6 cloth samples (2 x 2 cm, batch # 28, 48 % conversion) were attached to the glass frames with cotton thread and deployed as follows: one in each of the 4 flow chambers, one in the original flow chamber on top of the barrel and one submerged in a 1000 mL glass beaker in the barrel itself. Initial concentrations of Pb and Cu as determined with GFAA were 59 and 18.4 μg/Litre (0.285 and 0.289 μmol/Litre) respectively in ~ 190 litres at a pH of ~ 5.2. Linear velocities were measured as follows: 0.00131, 0.010, 0.185, and 0.252 cm/second in the 4 flow chambers, and

0.863 cm/second in the original flow chamber. The cloth pieces were deployed for a period of 24 hours after which they were removed and analyzed with λDXRF.

The results showing the dependence of the amount of Pb and Cu sorbed with respect to the flow rate are presented in Figure 25. It was observed that at very slow linear velocities (<0.3 cm/ second) there was little effect on the amount sorbed. However, as the linear velocity was increased to 0.863 cm/ second, the amount sorbed for both Cu and Pb was observed to increase. This dependence of the rate of sorption at 24 hours on the flow rate corresponds with the idea that diffusion through a surface boundary layer is part of the rate limiting step. It is noted that these flow rates were much slower than the maximum flow rates which might be observed in the environment where linear velocities of metres/ second can be observed.[85]

It was also observed that the initial molar amounts of Cu and Pb sorbed were similar, reflecting their almost identical molar concentration in solution. Along with the initial rates for Cu and Pb presented in section 4.1, these results support the idea that the initial rate of uptake for Cu and Pb, and perhaps for the majority of metals in solution, will be similar and directly related to their concentration in solution.

Figure 25. Effect of the Flow Rate on the Amount of Pb(II) and Cu(II) Sorbed from solution.

■ Cu, ● Pb
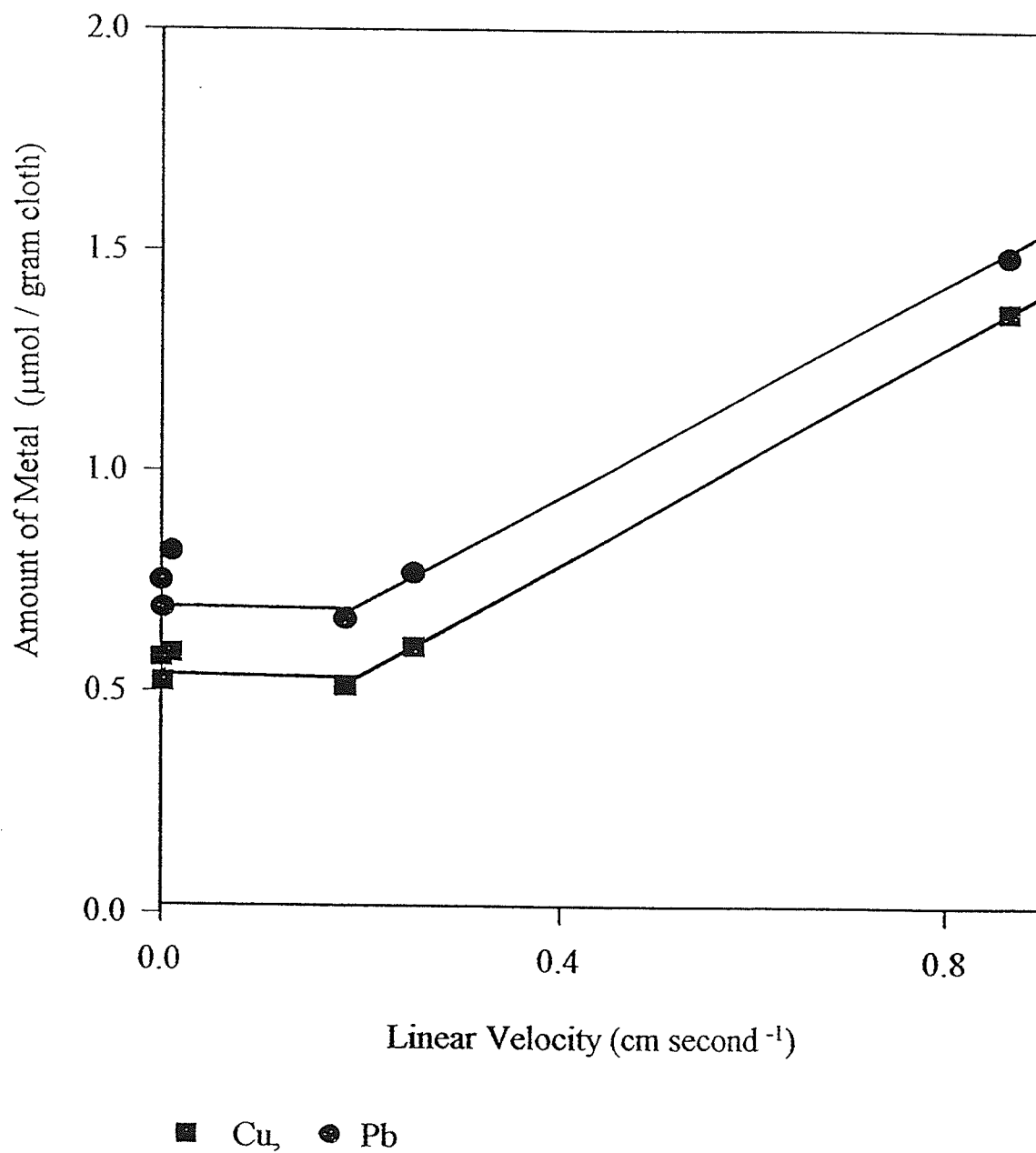
Initial concentration of Cu = 0.289 μmol/L
Initial concentration of Pb = 0.285 μmol/L

4.5   EFFECT OF INITIAL CONCENTRATION

The effect of the initial concentration of the metal in solution on the amount of metal taken up by the cloth monitors was investigated in a batch experiment using Pb(II). A series of 100-mL solutions were prepared consisting of 0.27, 2.17, 4.66, 6.32, 9.23 and 10.79 mg/Litre (1.3, 10.4, 22.5, 30.5, 44.5 and 52.0 µmol/Litre) in Pb(II), via serial dilution of a single stock solution of Pb(II), and adjusted to a pH of ~ 5.0 in 250 mL conical flasks. The initial concentrations of Pb(II) in the solutions were determined by AA. To each of the solutions were added two pieces of cloth (2 x 2 cm, batch # 28, 48 % conversion). The solutions were placed on a shaker for the duration of the experiment.

After 25.25 hours, one cloth piece was removed from each of the solutions, patted dry with a Kimwipe and allowed to air dry. Analysis of the metals sorbed was done by λDXRF. The results showing the amount of Pb sorbed with respect to the initial concentration of Pb(II) in solution are presented in Figure 26.

After 7 days had passed the remaining cloth pieces were removed from the solutions and analyzed for Pb content as described above, again with λDXRF. The results are presented in Figure 27.

Figure 26. Effect of the Initial Concentration of Pb(II)

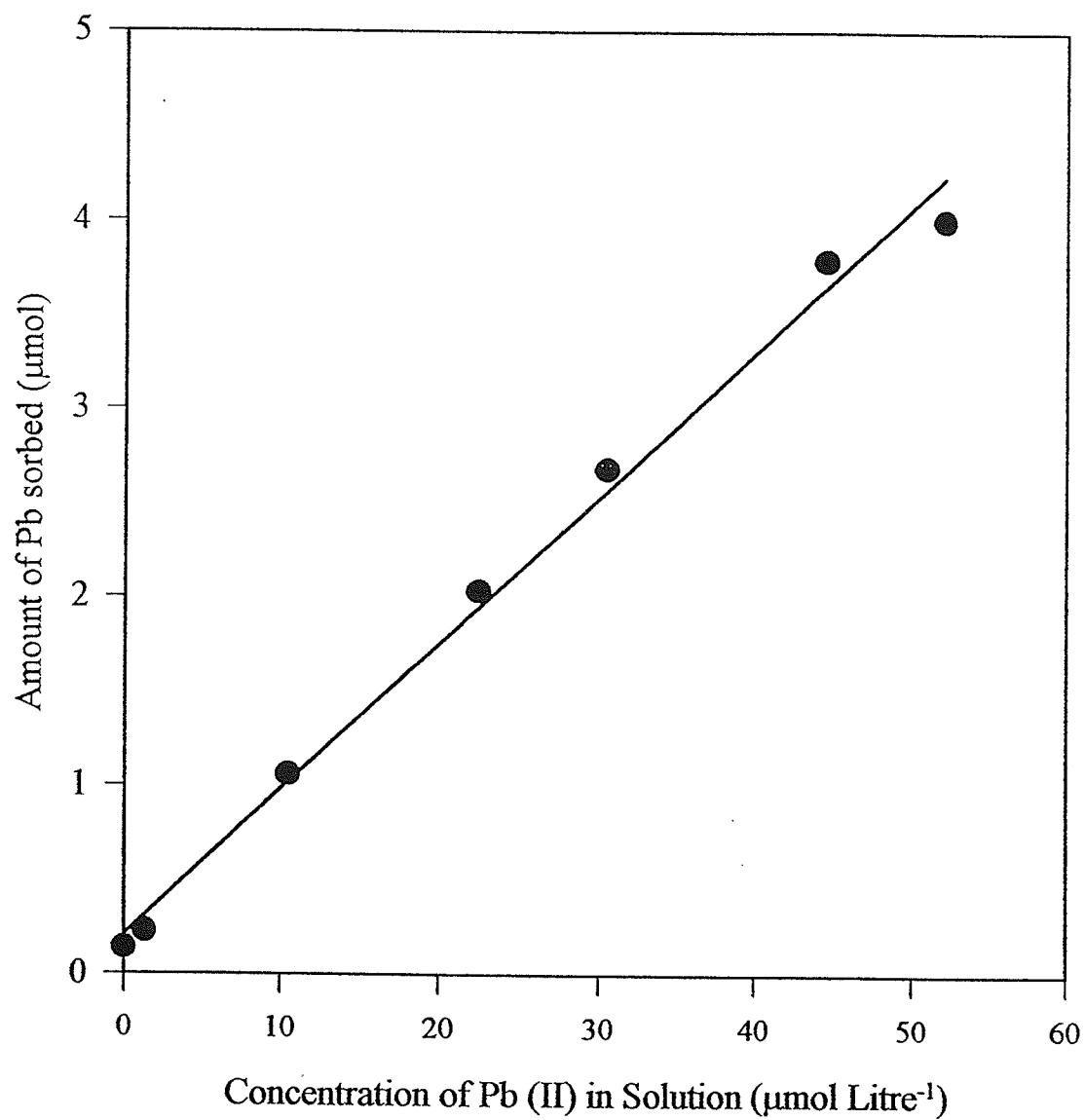on the Sorption of Pb(II)   (24 hour results)
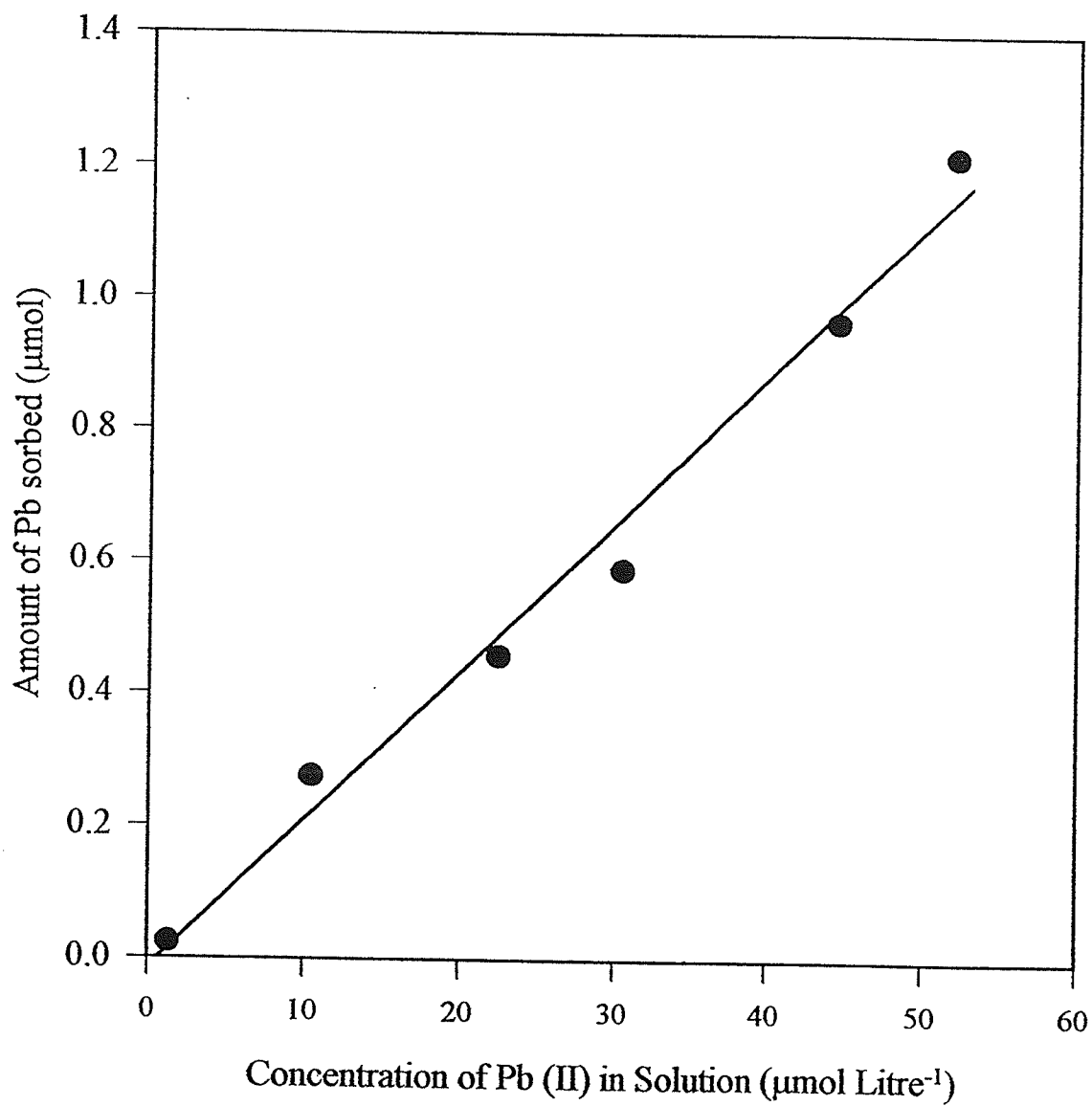
Figure 27. Effect of the Initial Concentration of Pb(II)

on the Sorption of Pb(II) (7 day results)

The solutions were then analyzed by AA for any Pb which may have still been present. The AA results indicated that the extraction of Pb from the solutions was essentially quantitative (>95 %) after 7 days. A material balance giving the concentrations of Pb, initially in solution, and sorbed on the cloth after 25.25 hours and 7 days is given in Table 5.

As λDXRF was used for the analysis of the cloth pieces after exposure, the amount of Cu present was measured as part of the routine analysis scheme. With the cloth pieces exposed for 25.25 hours there was no observable amount of Cu; however, with the cloth samples exposed for 7 days, a detectable amount of Cu was present on the cloth pieces. This indicated that Cu was present in a trace amount in the initial Pb stock solution. The amount of Cu sorbed by the cloth with respect to the initial Pb concentration is given in Figure 28.

From the results of 25 hours of exposure as shown in Figure 26, it was observed that the amount of Pb sorbed by the cloth pieces was linear with respect to the initial concentration of Pb(II). The linearity observed corresponds to the idea that the initial amount of metal sorbed is dependent

Table 5.   Material Balance for Pb.

Solution #	Amount of Pb analyzed in solution or on the cloth (µmol)					
	Initial /100 mL	Extracted 25.25 hours	Extracted 7 days	Remaining /100 mL	Total[1]	Degree of Extraction %
1	0.130	0.02	0.14	.11	0.36	18
2	1.05	0.28	0.23	.21	1.5	80
3	2.25	0.46	1.1	.11	2.6	95
4	3.05	0.60	2.0	.11	3.4	96
5	4.45	0.97	2.9	.10	4.9	98
6	5.21	1.22	4.00	.24	5.6	95

1)   The total amount of Pb was derived from the sum of the amount of Pb found on the cloth and the amount of Pb remaining in solution. The total value exceeds the original amount found in solution due to experimental error and rounding of results.

Figure 28. Effect of the Initial Concentration of Pb(II) on the Sorption of Cu(II)   (7 day results)
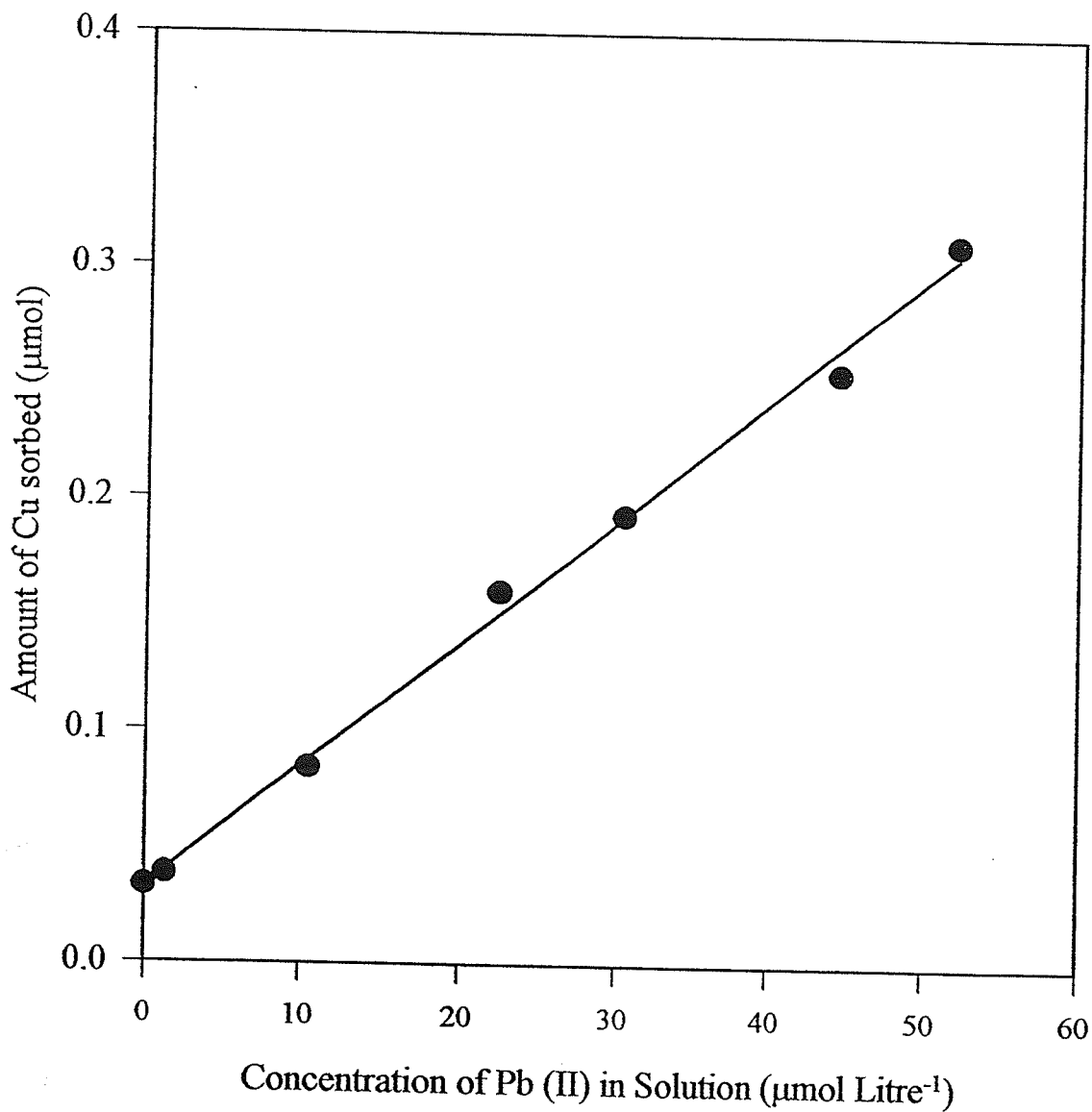
on the concentration of the metal in solution .[132]   Similar results were obtained for the samples of cloth exposed for 7 days. This was due to fact that the amount of Pb sorbed from solution was essentially quantitative.

The results of Figure 28 show the linear dependence of the amount of Cu sorbed with respect the initial concentration of Pb in solution. The linear dependence is due to the presence of a small amount of Cu in the original stock solution of Pb. As the solutions used were prepared by serial dilution, each solution received a trace amount of Cu in a fixed ratio to the amount of Pb present initially. The fact that Cu was sorbed supports the idea that the amount of surface chelating groups was greater than the amount needed to complex all of the metal present in solution.

Because adsorption was linear, the development of equations relating the amount of metal sorbed by the cloth, when placed in the environment, will be easier. It is noted that in the case of the 24 hour results for Pb that when the concentration of Pb was doubled from ~20 to ~40 mmol/L that the amount sorbed doubled as well from ~0.4 to ~0.8 µmol/ piece of cloth.

4.6   CAPACITIES FOR Pb AND Cu / 24 HOURS, 7 DAYS

The effect of a large excess concentration of metal in solution on the amount of metal sorbed by the cloth, was investigated using Pb(II) and Cu(II). From this experiment an estimate of the capacity of the cloth for Cu(II) and Pb(II) was calculated.

A solution of 100 mL ~ 0.2 mol/L in Pb(II) was prepared and adjusted to pH = 5.0, in a 250 mL conical flask. A total of four cloth pieces, two each from batch # 23 and # 28 (46 and 47 % conversion respectively) were placed in the solution which was then placed on a shaker. After a period of 24 hours two of the cloth pieces, one each from batches # 23 and # 28, were removed, patted dry with Kimwipes and dried in air. Analysis of the metals sorbed was done by acid extraction of the cloth, followed by AA. The remaining two cloth pieces were removed after 7 days of exposure and analyzed in a similar manner.

The same procedure was used for the Cu analysis. A solution of 100 mL ~ 0.2 mol/L in Cu(II) was prepared and adjusted to pH = 4.5 in a 250 mL conical flask. Two cloth pieces, one each from batches # 23 and # 28 (46 and 47 % conversion respectively) were placed in the solution which was then placed on a shaker. After 24 hours, the cloth pieces were removed and

analyzed as described above.

A slightly different procedure was used for the extended time of exposure of 7 days. A series of solutions of 100 mL each, 0.04 mol/L Cu(II) were prepared and adjusted to pH = 5.0. Two cloth pieces, one each from batch # 23 and # 28 (46 and 47 % conversion respectively) were placed in one of the solutions on a shaker for a period of ~ 48 hours. The cloth pieces were then removed and placed in a fresh solution of Cu(II) for 24 hours. The process was repeated until a total time of exposure of 7 days had passed, after which the cloth samples were dried and analyzed as described above.

The results showing the amount of Pb and Cu present on the cloth pieces after 24 hours of exposure are presented in Table 6. From the initial results, at 24 hours of exposure the amounts of Pb and Cu sorbed were found to be quite high, indicating a relatively rapid rate of uptake from the concentrated solutions. It is noted that the amounts sorbed are ~ 1/5 of the total theoretical capacity assuming a 1:1 complex being formed. The results for the 7 days of exposure are presented in Table 6 and are slightly different from the 24 hour results. In this case the total amount of Pb sorbed is greater than the amount of Cu sorbed.

Table 6. Capacities of cloth for Cu and Pb exposed for 24 hours.

cloth used	amount sorbed mg/ 4 cm² piece		amount sorbed mmol/ gram		% theoretical capacity [1]		% theoretical capacity [2]	
batch, %	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
23, 46	7.9	16	1.2	0.79	22	14	44	28
28, 47	9.9	17	1.6	0.85	27	15	54	30

1) Theoretical capacity of 5.66 mmol/ gram cloth was calculated from the weight % of amidoxime groups / gram of cloth, assuming a 1:1 complex.

2) Theoretical capacity of 5.66 mmol/ gram cloth was calculated from the weight % of amidoxime groups / gram of cloth, assuming a 1:2 complex.

3) Conditions were pH = 5.0 and 4.5 for Pb and Cu solutions respectively.

Table 7. Capacities of cloth for Cu and Pb exposed for 7 days.

cloth used	amount sorbed mg/ 4 cm² piece		amount sorbed mmol/ gram		% theoretical capacity[1]		% theoretical capacity[2]	
batch, %	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
23, 46	5.9	33	0.93	1.59	16	28	32	56
28, 47	7.1	45	1.12	2.17	20	38	40	66

1) Theoretical capacity of 5.66 mmol/ gram cloth was calculated from the weight % of amidoxime groups / gram of cloth, assuming a 1:1 complex.

2) Theoretical capacity of 5.66 mmol/ gram cloth was calculated from the weight % of amidoxime groups / gram of cloth, assuming a 1:2 complex.

3) Conditions were pH = 5.0 for both Cu and Pb solutions.

The difference in the amount of Cu and Pb sorbed may be attributed to a difference in the number of chelating groups bound to the metal. In the case of Pb a 1:1 chelate complex with amidoxime is preferred while in the case of Cu, two amidoxime groups are preferred.[122] This corresponds to the 7 day results given in Table 7 where the capacity of the cloth for Pb of 2.17 mmol/gram is almost double the capacity for Cu of 1.12 mmol/gram. This set of results supports the idea presented earlier that Cu and Pb are taken up by a slightly different mechanism by the cloth. The net result from this is that there are a greater number of single amidoxime sites on the surface of the cloth than the number of sites in which two or more amidoxime groups are close enough in space to allow for the formation of multiple chelate complexes.

4.7   TEMPERATURE EFFECT

In the environment, the temperature of an aqueous system can be expected to vary considerably; therefore, the effect of temperature on the amount of metals taken up by the cloth was investigated. A solution of 8.82 mg/Litre (43 μmol/L) in Pb(II) was prepared and adjusted to a pH of ~ 5.2. Cloth pieces (2 x 2 cm, batch # 30, 47 % conversion) were placed in 100

mL each of the stock solution. The solutions were stirred via magnetic stirrers on hot plates at the following temperatures: 9, 31, 37, 60.5 °C, for a period of 24 hours. After exposure the cloth samples were dried in air. The amount of Pb sorbed was determined by AA analysis of the remaining solution.

The results showing the amount of Pb initially sorbed at the different temperatures are given in Figure 29. There was an observable effect of the temperature on the initial rate of Pb sorbed, over a temperature range which might be found in the environment. Because of this, the use of the cloth as a monitor would require measuring the temperature of the sample site.

An Arrhenius plot of the initial rate of sorption is given in Figure 30. The linear fit presented was derived using Table Curve, with a correlation coefficient >0.970. From the slope the activation energy of the sorption of Pb(II) was calculated to be ~ 32.9 kJ/mol (7.86 kcal/mol). This value is in agreement with values derived for the bond strengths between metals and chelating resins which range from ~ 2-3 kcal/mol for purely ionic interactions to ~ 15-25 kcal/mol for chelate formation.[133] The pre-exponential factor was calculated to be ~ 1000 sec^{-1}.

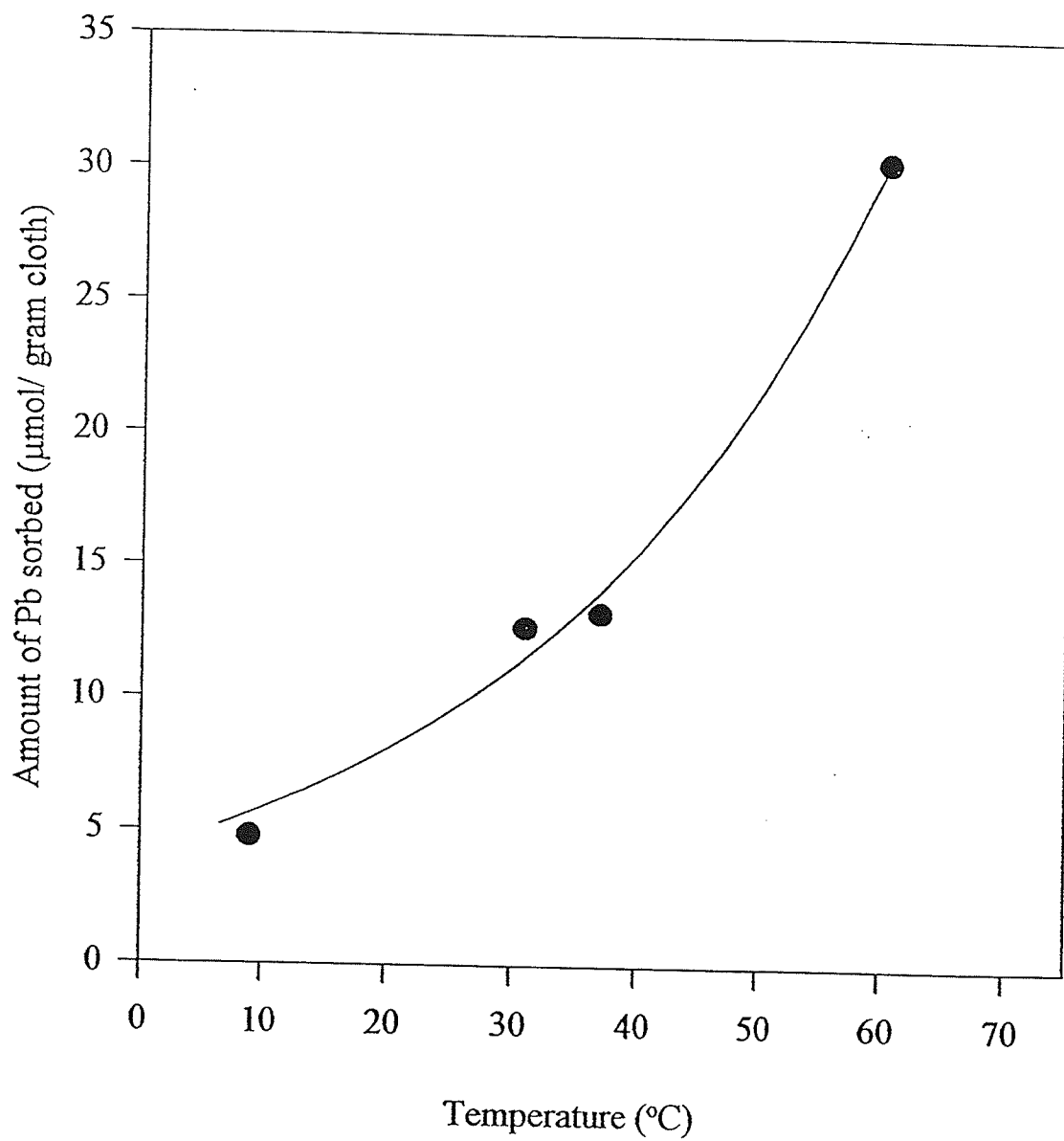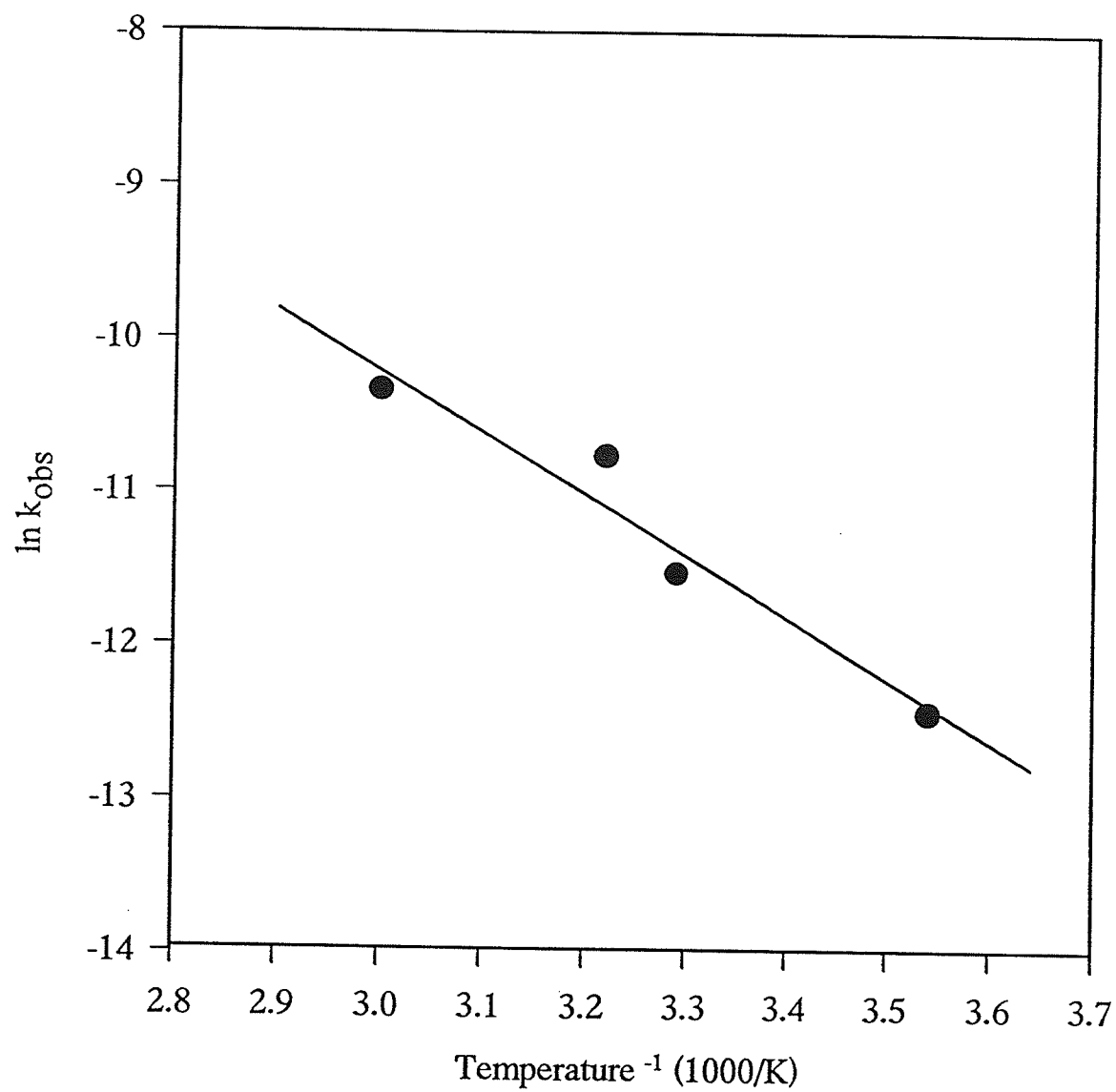Figure 29. Effect of Temperature on the Amount of Pb(II) Sorbed

Figure 30. Arrhenius Plot for Pb(II) Sorption

4.8 COMPETING METALS Pb AND Cu

In order to further understand the processes involved in the sorption of metals from solution, and to determine if the rate of sorption would be affected by a competing process between different metals for surface chelating groups, an experiment was performed in which an increasing excess of Cu(II) was placed in solution with a fixed amount of Pb(II).

Cloth samples (2 x 2 cm, batch # 30, 47 % conversion) were placed in 250 mL conical flasks containing 100 mL of 0.1, 2.0, 9.9, 20, 50, and 100 mg/L (0.16, 3.18, 15.5, 31.9, 78.7, and 157 μmol/L) of Cu(II) prepared via serial dilution of a stock solution of 1000 mg/L in Cu(II). To each flask 0.65 mL of a 1000 mg/L solution of Pb(II) was added to produce an average concentration of Pb in each solution of 0.65 μg/L (3.14 μmol/L). The samples were covered with Saran wrap and shaken for 24.5 hours. The concentrations of Cu and Pb in each flask were determined by AA before exposure and in the case of Pb, after exposure as well. The amount of Pb sorbed by the cloth was determined by acid extraction of the cloth followed by AA analysis.

The ratio of the amount of Cu to Pb initially in solution is given in Table 8, and shows that the amount of Cu present in solution varied from an amount similar to the amount of Pb to an amount which was substantially greater than the amount of Pb. The amount of Pb sorbed by the cloth with respect to the increasing amount of Cu in solution is given in Figure 31. The increasing amounts of Cu were observed to have no effect at all on the initial amount of Pb sorbed by the cloth. This set of results suggests that there was no inhibitory effect for the sorption of Pb due to Cu under these conditions. This can be extrapolated by stating that due to the large amount of surface functional chelating groups present being much greater than the amounts of metal in solution, that any inhibitory or competitive effects that one metal may have on the sorption of another metal may be considered to be negligible.

4.9   DESORPTION OF METALS

The amount of metal desorbed from the cloth as a function of the time was investigated. This was carried out by measuring the amount of Pb present on a piece of cloth, which was initially doped with Pb(II), before and after exposure to a flow of clean water.

Table 8. The Amount of Cu Present in Solution with Respect to Pb.

Solution	Amount of Cu		Amount of Pb		Cu / Pb
	mg/L	μmol/ 100 mL	mg/L	μmol/ 100 mL	mole fraction
1	0.10	0.157	5.90	2.85	0.05
2	2.02	3.18	5.34	2.58	1.2
3	9.88	15.5	6.30	3.04	5.1
4	20.3	31.9	6.65	3.21	9.9
5	50	78.7	6.52	3.15	25
6	100	157	6.67	3.22	49

Figure 31. Effect of Excess Cu(II) on the Amount of Pb(II) Sorbed
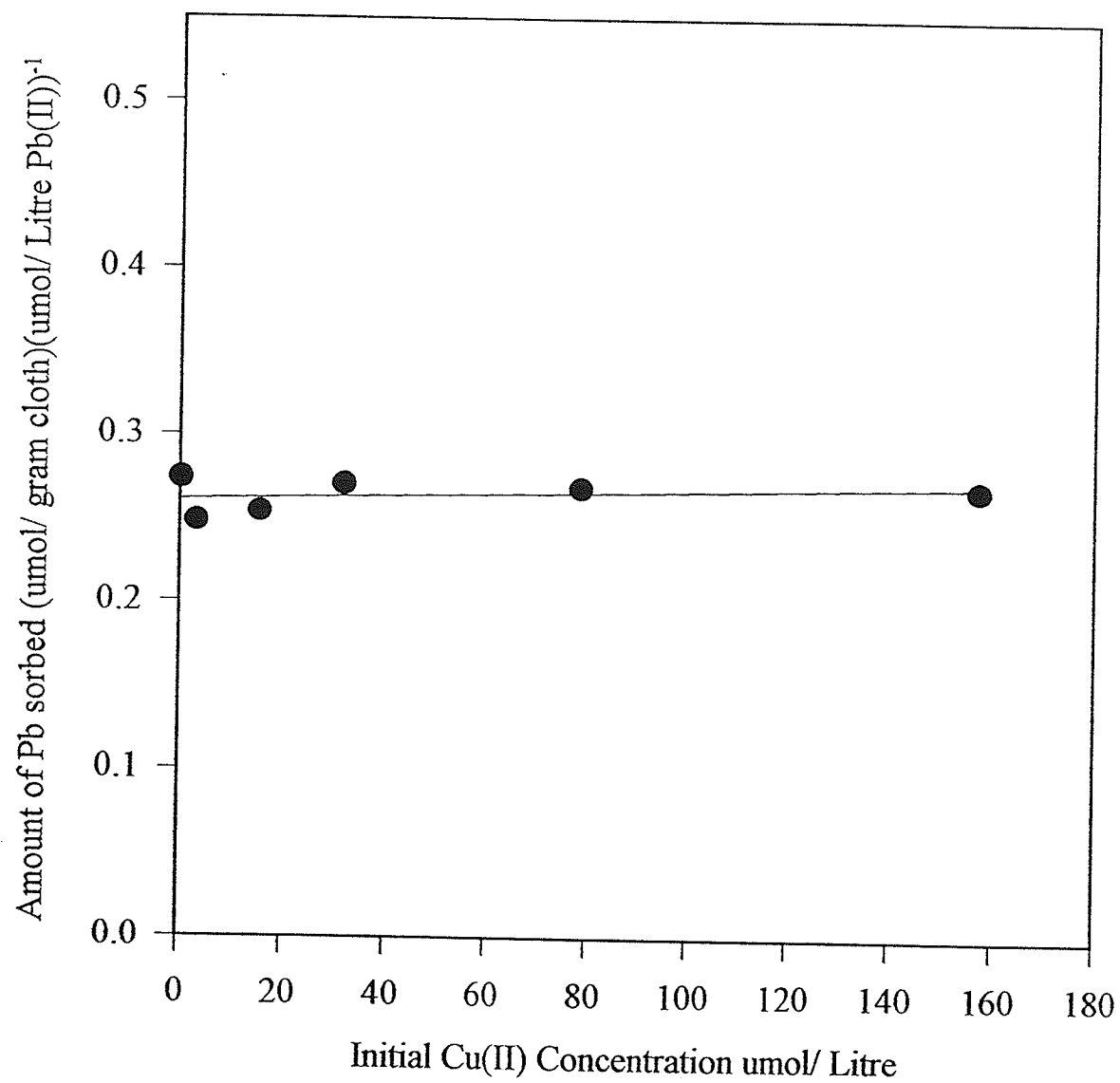
The flow system shown in Figure 4 was used to ensure that the resorption of Pb would not occur by supplying a constant feed of fresh water (ro). A total of 8 cloth pieces (2 x 2 cm, batch # 30, 45 % conversion) were exposed to 100 mL of a solution of ~ 10 mg/Litre (48 µmol/L) in Pb(II), at a pH of ~ 5.2, for a period of 36 hours in order to sorb Pb(II). The cloth pieces were then removed from solution, patted dry with Kimwipes and allowed to dry in air.

After the sorption of Pb(II), 6 of the cloth pieces were attached to the glass frame used and placed in the flow chamber. One of the remaining two cloth pieces was rinsed three times with water (ro, nanopure) and allowed to air dry, while the other cloth piece was not further processed. At varying times of desorption, the cloth pieces were removed from the flow chamber, patted dry with Kimwipes, and dried in air. Analysis of the amount of Pb present on the cloth was done by acid extraction followed by AA.

The effect of the time of exposure to clean water on the amount of Pb desorbed by the cloth is presented in Figure 32. It was observed that there was an initially large decrease in the amount of Pb present on the cloth (~ 20 %) which then slowed and reached a limiting value after 18 hours.

Figure 32. Effect of the Time of Exposure on the Amount of Pb Desorbed
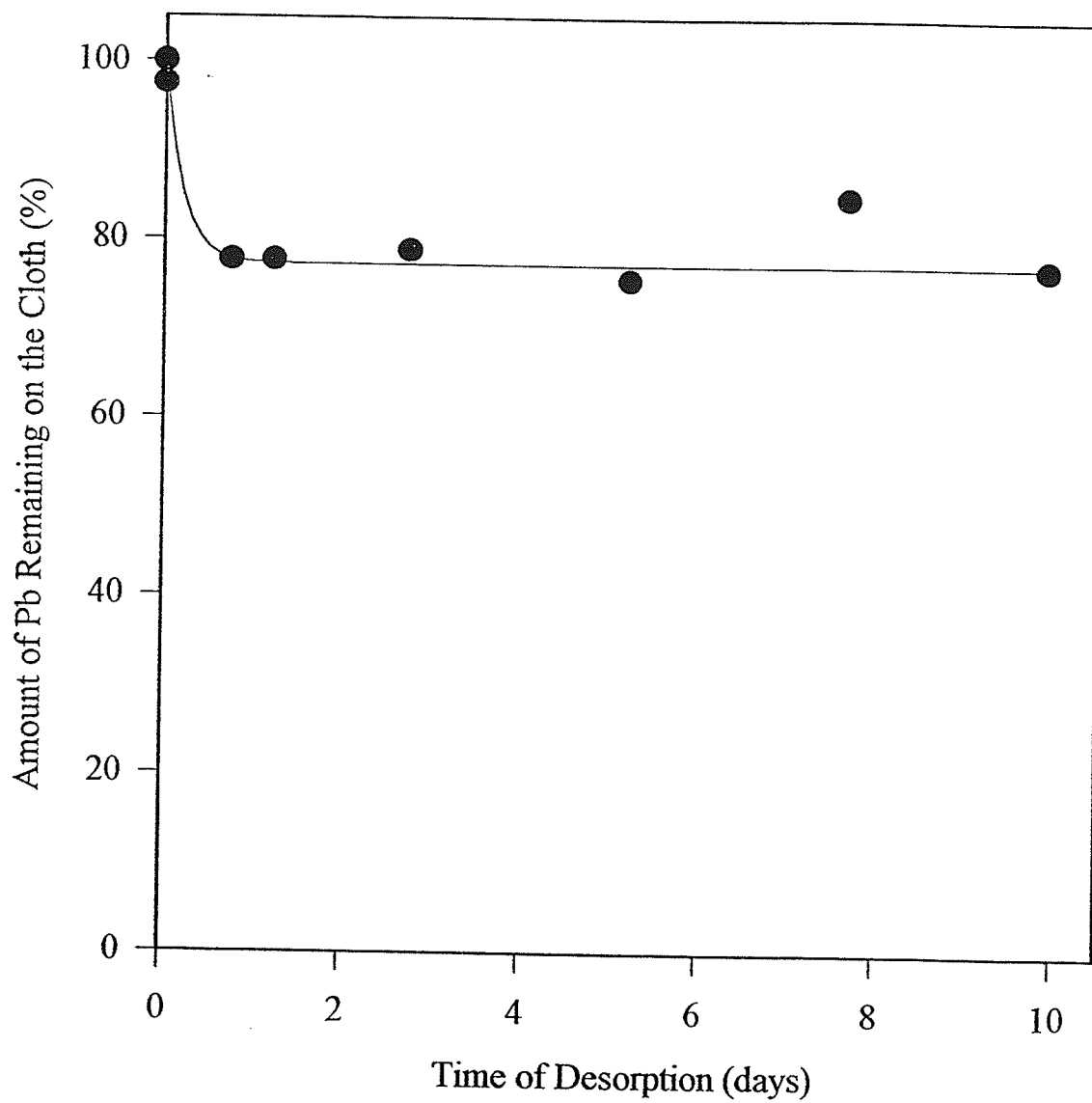
The rapid initial rate was presumed to be due to the loss of Pb which was not chelate bound and/or the loss of Pb near the surface of the cloth. The fact that the amount of Pb desorbed levelled off suggests that the initial Pb desorbed was entirely from the surface and that the Pb present within the cloth would not desorb as easily as there was less contact with solution. Another possible factor is that within the interior of the cloth the amidoxime groups may be in closer proximity to each other and thus the formation of a multiple complex may be favoured. It was initially presumed that the amount of metal desorbed by the cloth would be negligible due to the slower kinetics of desorption. This is something which is observed in resin kinetics, where the increase in the rate of desorption from a column is achieved by adjusting the solution pH to a relatively low value of ~ 1, something which is unlikely to happen naturally in the environment.

4.10 USE OF AN INTERNAL STANDARD

The use of an internal standard was investigated as a means of simplifying the quantitation of analysis and a means of increasing the accuracy of the results. Two different approaches were investigated with respect to the type and choice of the internal standard.

The first approach investigated consisted of doping the cloth with a metal, in this case Au(III), as it forms a strong chelate complex with the amidoxime group and thus would be favoured not to desorb during deployment.[83,108] Three cloth pieces (2 x 2 cm, batch # 26, degree of conversion = 42 %) were doped with Au(III) via exposure to a solution of 100 mL in 50 mg/Litre Au(III) for 60 minutes. The cloth pieces were then removed and allowed to dry in air. Analysis of the amount of Au present on the cloth was done by λDXRF. One of the cloth pieces was then exposed to ~ 1 Litre of tap water for a time of 24 hours. The second piece was exposed to ~ 1 Litre water derived from the hot water supply, again for 24 hours. The third piece was not further processed. After exposure, the three cloth pieces were reanalyzed by λDXRF.

The second approach to the choice of an internal standard was based on the presence of TiO_2 in the original Orlon cloth. The metal in this case was physically bound within the fibres themselves and would not be expected to desorb into solution during exposure, something which may occur with a chelated metal. The question as to whether or not the Ti present desorbed from the cloth during exposure was investigated. A total of 15 cloth pieces (batch # 5, ~ 30 % conversion) were placed in the original

flow chamber used previously, for times of 4, 7, 11 and 15 days. After exposure the cloth pieces were dried in air and the amount of Ti present analyzed with EDXRF.

The results depicting the use of Au as the internal standard, showing the peak intensities for Pb, Cu and Au recorded before and after exposure, are shown in Table 9. It was observed that the initial values for Au fluorescence were essentially the same, within ~ 3 % of each other. The pieces of cloth were also found to have trace amounts of Cu and Pb present.

After exposure to the tap water solutions, the amount of Au was observed to decrease in the samples compared with the unwashed sample. The effect was more pronounced for the cloth placed in hot water which suggests that the desorption process was endothermic. It was also observed that a substantial amount of both Cu and Pb were sorbed. These results indicated that the use of a metal bound to the cloth via chelation, even one as strongly bound as Au, would not be suitable for use as an internal standard, because the metal could come off of the cloth during exposure.

The results showing the EDXRF intensities for Ti with respect to the time of exposure are shown in Figure 33. The error observed was ~ 5 % in the replicate measurements. As with the previous results with Au, the mean

Table 9. Results for Au(III) as an Internal Standard

Solution	Net intensity λDXRF, after doping with Au(III)			Net intensity λDXRF, after exposure to water		
	Au	Cu	Pb	Au	Cu	Pb
blank, not treated	370	330	15	380	330	0
cold tap water	380	330	0	320	1280	0
hot tap water	360	320	0	240	710	180

Figure 33. Variation of TiO$_2$ With Respect to the Time of Exposure
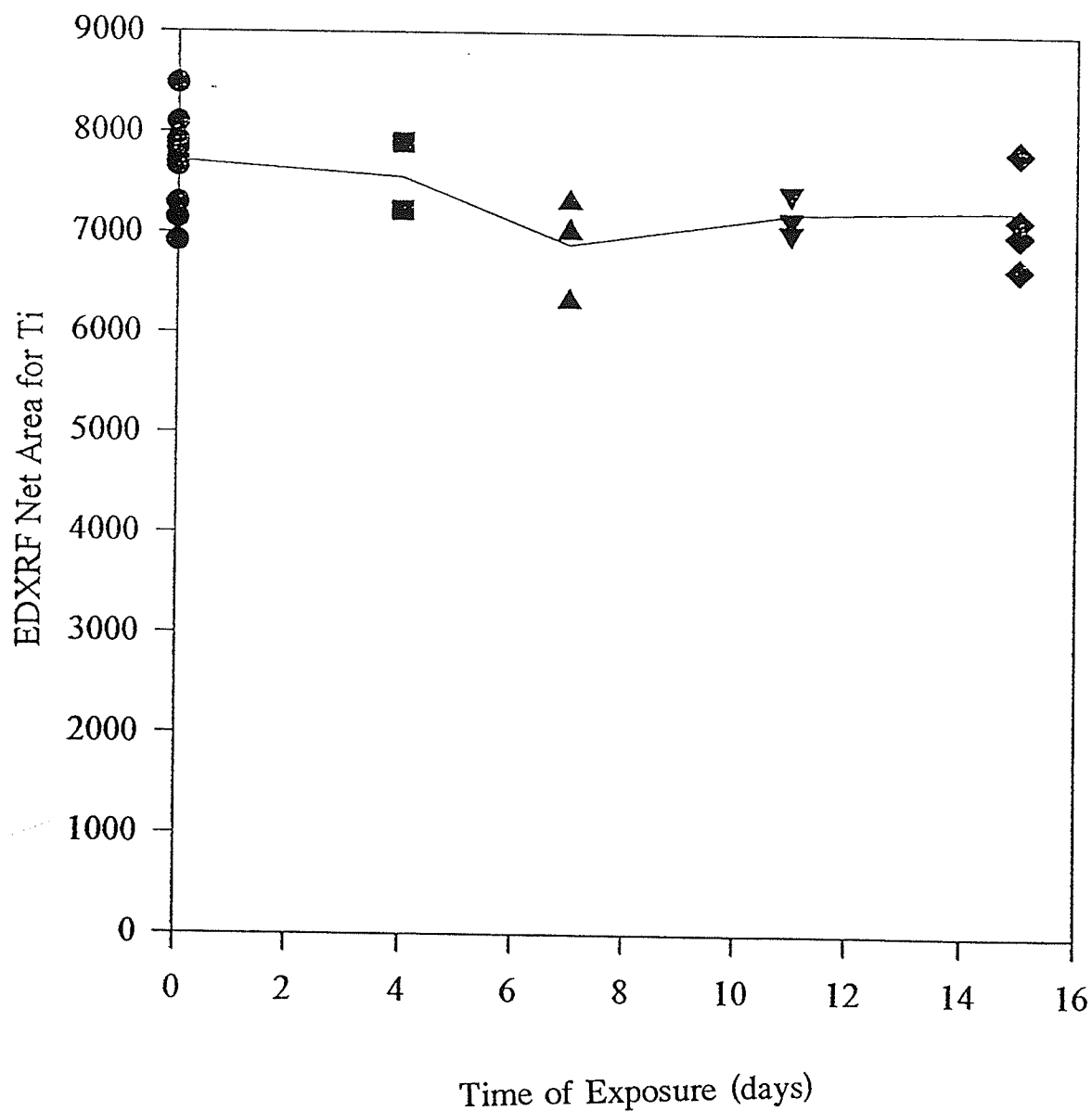
amount of Ti was observed to decrease during exposure. However, in this case, the decrease was observed to be in the range of only ~ 6 % of the original value, which was a relatively small change. The loss of TiO_2 was presumed to be purely a physical loss from the particles bound within the fibers of the cloth, and not due to a chemical process such as the desorption of a chelate bound metal, as was the case for Au. These results suggest that TiO_2 would be suitable for use as an internal standard for the cloth as it does not come off rapidly and could also provide for a measure of determining the absolute error in measurements of replicate samples.

4.11 CONDITIONING WITH HCl

Treating the cloth with a dilute solution of HCl was done in order to observe the effect of acid treatment on the physical properties of the cloth, and on the resulting uptake of metals from solution. Pieces of cloth (batch # 13, ~ 62 % conversion) were placed in 200 mL of ~ 1.2 M solution of HCl for 5 and 30 minutes. The monitors, along with ones that were not treated with HCl, were then exposed to the flow chamber. The conditions were the same as those used for the kinetics experiment given in section 4.1, with a period of exposure of 64 hours. After the sorption of Pb(II), the cloth pieces

were rinsed with water (r.o.) and patted dry with Kimwipes before analysis.

The effects of the treatment of the cloth with HCl were extended to a number of the field tests using the passive monitors. After the preparation of a standard monitor using cloth from batch # 25, 73 % conversion, the entire monitor, both cloth and the plastic frame, were placed in ~ 0.1 M HCl for 5 minutes. After treatment the monitors were rinsed with water (ro, nanopure) and allowed to dry before deployment. The monitors were used in the field tests in Beaver Creek and the results are presented in the section on field tests.

The EDXRF spectra of the cloth before and after 5 and 30 minutes of treatment in HCl is shown in Figure 34. It was observed that although the cloth was washed after the treatment process, there was a detectable amount of Cl present which suggested that the amine part of the amidoxime group was in its protonated form. During the course of treatment with HCl the cloth was observed to swell considerably and then collapse after washing with water. The physical properties of the cloth were observed to degrade with the HCl treatment. It is noted that there was no discernable difference in the cloth treated for 5 minutes compared with the cloth treated for 30 minutes.

Figure 34. EDXRF Spectra recorded on Monitors Before (lower)
and After Treatment in HCl for 5 (middle) and 30 (upper)
Minutes.
Peaks correspond to Cl and Ti at 40 and 120 channel
numbers respectively.

Counts

Channel Numbers
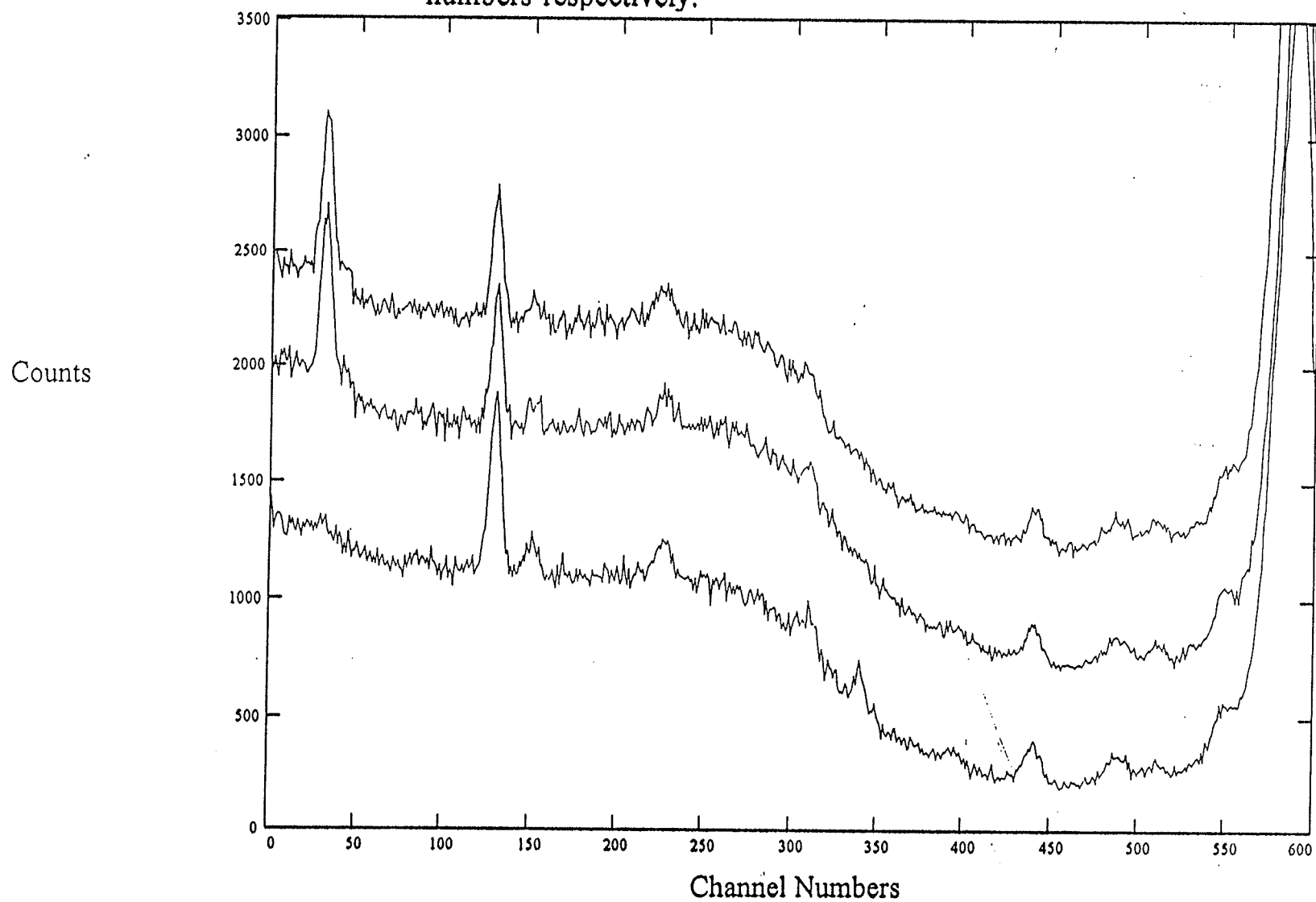
The EDXRF spectra recorded on the HCl-treated cloth and untreated cloth after exposure to the flow chamber are shown in Figure 35. It was observed that after exposure there was a complete loss of the Cl peak as the remaining HCl was presumably removed from the cloth into solution. It was also observed that the amounts of Cu and Pb sorbed by the treated cloth were greater than the amount taken up by the untreated cloth. This was due to the treatment process in which the amine groups were protonated, which resulted in the cloth becoming more hydrophillic and thus decreased the resistance to solvation by water. The net result was a reduction in the boundary diffusion layer between the cloth and solution. This ultimately allowed more solution to flow within the confines of the fibres within the cloth.

These results are similar to the observations made with respect to an increase in the amount of metals sorbed because of an increase in the hydrophillicity of a fibre.[90,118,119] The HCl treatment, although it produced a better cloth with respect to the amount of metals sorbed, resulted in the partial degradation of the cloth and thus was not further investigated.

Figure 35. EDXRF Spectra recorded on an Untreated Monitor (lower), and HCl Treated Monitors (5 minutes, middle and 30 minutes, upper) After Exposure to the Flow Chamber.
Peaks correspond to Ti, Fe, Cu, Zn and Pb at 120, 220, 320, 340, and 440 channel numbers respectively.
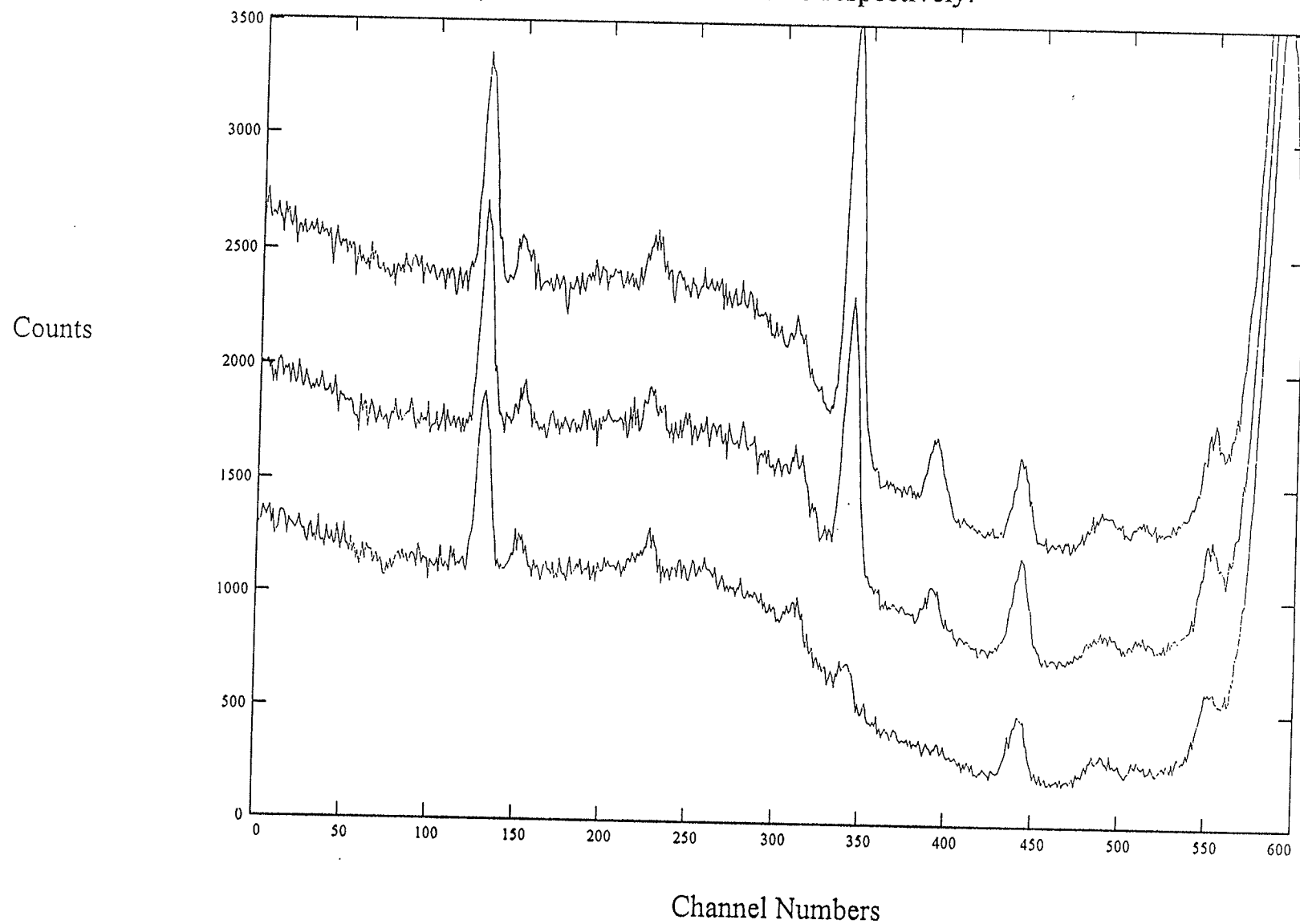
4.12 CONDITIONING WITH NaOH, NH$_4$OH

Conditioning of the converted cloth with dilute NaOH and NH$_4$OH was carried out in order to investigate the resulting effects on the uptake of metals and the physical properties of the cloth. For the NaOH and NH$_4$OH treatment, small pieces of converted cloth (2 x 2 cm, batch # 24, 21 % conversion) were placed in ~ 200 mL of a 0.1 M solution of either NaOH or NH$_4$OH for periods up to ~ 8 hours. The treatment was carried out at room temperature and the solutions were rapidly stirred. Cloth pieces were removed from the solution during the course of treatment and washed with water (ro) and then dried.

After treatment with base, the cloth pieces were placed in a 0.1 M solution of HCl for 10 minutes and then washed with water (ro). The HCl wash was repeated twice more for 1 minute intervals followed by rinsing in water (ro) until the water remained neutral. The cloth pieces were then grouped together and placed in 250 mL of a dilute solution of Pb(II) , [Pb(II)] = 60 mg/L (290 μmol/L), at pH ~ 5.0, for 5 hours on a shaker so that sorption of Pb(II) could occur. After sorption, the cloth pieces were rinsed in water (ro) and patted dry with Kimwipes. Analysis of Pb(II) taken up was done by acid extraction followed by GFAA.

During the treatment process with NaOH, the cloth was observed to become progressively yellow/orange in color as the length of treatment increased. This was presumed to be from the Na^+ ions present on the cloth, as the NH_4OH treatment produced no noticeable color change. After washing in dilute HCl, the cloth returned to its original white color and was observed to swell slightly.

The results are presented in Figure 36 for NaOH and NH_4OH treatment. It was observed that both the NaOH and the NH_4OH treatments resulted in a decrease in the amount of Pb initially sorbed by the cloth. The slight difference in the effect of NaOH versus NH_4OH was due to the increased base strength of NaOH. It is noted that these results were contradictory to previous findings in which the amount of $UO_2(VI)$ sorbed generally increased with an increasing time of alkaline treatment.[99,100,105,106] The differences were presumed to be due to the differences in the physical properties of the cloth compared with the fibers used for the sorption of $UO_2(VI)$ in which the degree of conversion of the fibre was ~ 100 %. Additionally, in this case Pb(II) was studied and not $UO_2(VI)$.

Figure 36. Effect of Alkaline Treatment on the Sorption of Pb(II)
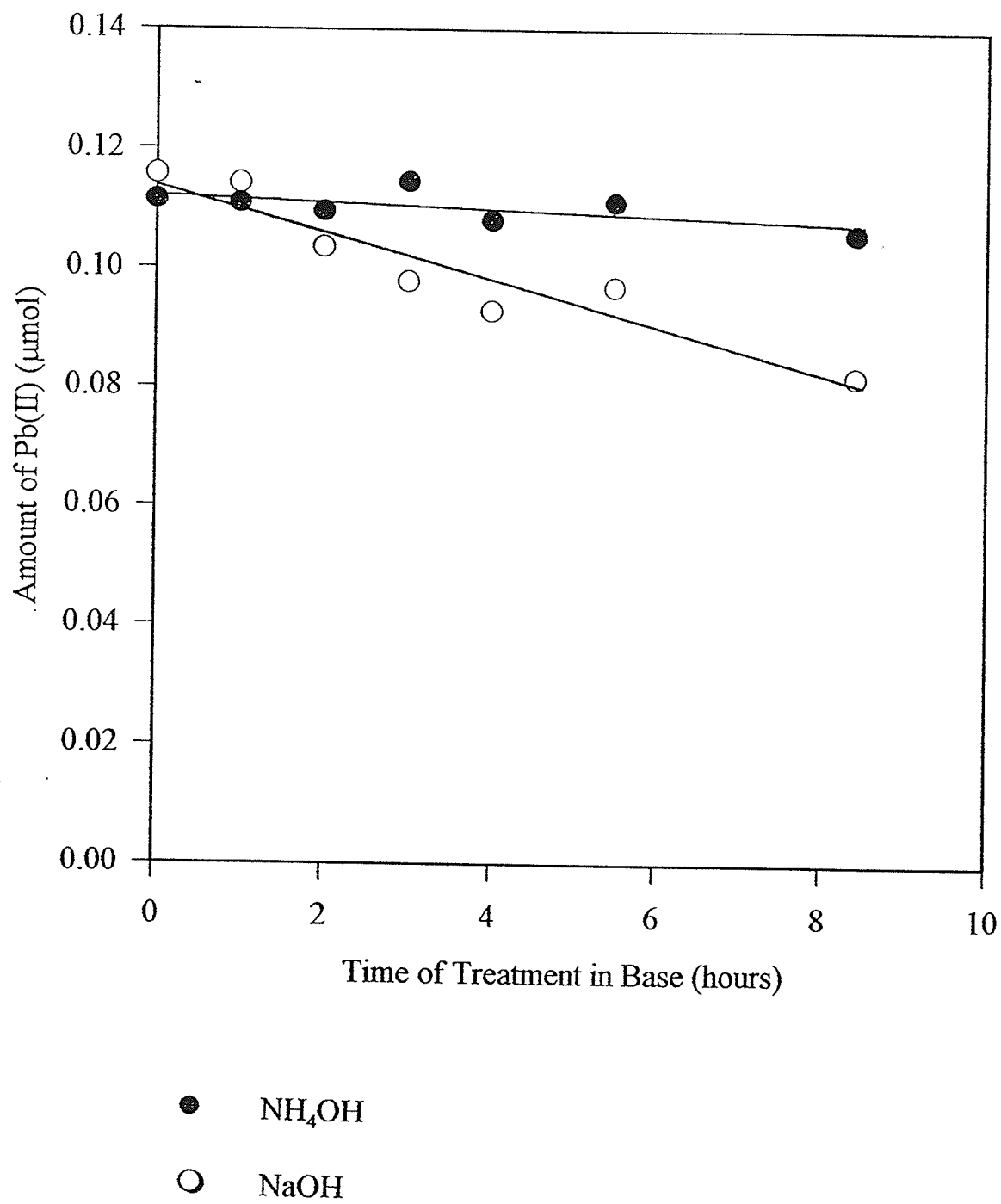
4.13 SUMMARY

In summary, the use of the flow chambers as a means to simulate the conditions of environmental sampling was successful in providing an idea of some of the factors which would influence the amount and rates of metals sorbed by the cloth, as did some of the bath experiments. The *in vitro* experiments demonstrated the feasibility of the passive *in situ* sorption of trace metals by the cloth followed by either λDXRF or EDXRF analysis. A sensitivity in the ppb and sub ppb range, and a precision better than 6 %, suggests that this method was observed to be adequate for environmental analysis. As well, a correlation was drawn between the cloth and previous work with fibers and resins containing amidoxime chelating groups.

Use of EDXRF and λDXRF as the methods of analysis for metals bound to the cloth proved to be relatively easy and sensitive. It was found that the EDXRF instrumentation was easier to use but was not as sensitive as the λDXRF instrument which used a tube as the X-ray source. It was also observed that due to the high intensity of the tube source used in the λDXRF instrument the cloth samples changed in appearance. This was attributed to a radiation-induced reaction within the cloth such as fusing or cross-linking.[98] The result of this was the reduced possibility of reusing the

monitors for more than one deployment and analysis.

Thus it was found that the physical properties of the cloth made it suitable for use in the passive monitors deployed in the field tests.

FIELD TESTS

5   INTRODUCTION

In order to evaluate the practical application of the chelating cloth as a passive monitor a number of field tests were performed. The locations were chosen in an attempt to provide as varied conditions as possible for sampling. A number of factors were investigated including the deployment of samplers by untrained personnel, mailing of the samplers to the laboratory for analysis, use of filters to reduce particulate matter sorbed onto the sampler, the effects of water conditions such as flow rate, turbidity and sample location with respect to the shore and the surface of the water.

During the course of the limited field testing of the monitors, a great deal of information was gained as to the practicality of using the cloth as a passive monitor for trace metals in water. Deployment of the monitors proved to be relatively easy, especially when a fishing rod was used to cast the monitor to a specific location from the shore. However, collection of the monitors after deployment produced some of the most disappointing results. This was due to the fact that the monitors were often removed from the sample location, most likely by persons passing by, presumably through

curiosity. A total of 24 monitors which were deployed at the sample locations mentioned here were lost. This lead to the deployment of monitors at more remote locations unlikely to be frequented by the general public, as well as the camouflaging of the monitors and anchor line.

## 5.1 RED RIVER, UNIVERSITY OF MANITOBA

The first field test of the performance of the monitors was carried out by placing several monitors in the Red River near the University of Manitoba, Winnipeg, Manitoba., in the spring of 1994. Several monitors (batch # 1, 10 % conversion) were attached with monofilament fishing line to a Nylon rope which had a large weight on one end to act as an anchor and a Styrofoam block on the other end to act as a float. Deployment was carried out with the use of a small inflatable boat. The anchor and rope were dropped ~ 3 meters from the shore in about 1.5 meters of water. At the time of deployment the water was observed to be very murky or turbid and the flow rate was considered to be fast.

During the course of exposure the water level was observed to have dropped by ~ 1 meter. After 7 days of exposure the monitors were found on the shore, out of the water. Several of the monitors were contaminated with

soil and other organic matter. All of the monitors were rinsed in water (ro) before analysis to remove the bulk of soil and organic matter that was deposited on them. After drying in air, the monitors were analyzed by EDXRF. An acquisition time of 1000 seconds was used. Blank spectra were recorded on the monitors before deployment for comparison.

A sample EDXRF spectrum recorded on one of the monitors, before and after exposure to the Red River is shown in Figure 37. After comparison with the blank spectrum, it was observed that the spectrum of the monitor after exposure had a number of peaks which corresponded to the presence of sorbed metals, as well as metals found in sorbed particulate matter. The largest peak was observed to be due to the presence of Fe. This was not unexpected as Fe is known to chelate well with the amidoxime group and is found in relatively large amounts in environmental waters as well as in humic material.[123] Other metals sorbed were Cu, Ni, Ca and a trace amount of Pb. The sorption of Ca was presumably due to the large amount of Ca present in the river water. Generally, Ca is several orders of magnitude greater in concentration then the trace metals present. The presence of secondary structures on the surface of the cloth would account for the sorption of Ca, as the amidoxime group is known to not sorb the

Figure 37. EDXRF Spectra Recorded on a Monitor Before (lower) and
After (upper) Deployment in the Red River.
Peaks correspond to Ti, Fe, Ni, Cu and Pb at 120, 220, 270, 320
and 470 channel numbers respectively.
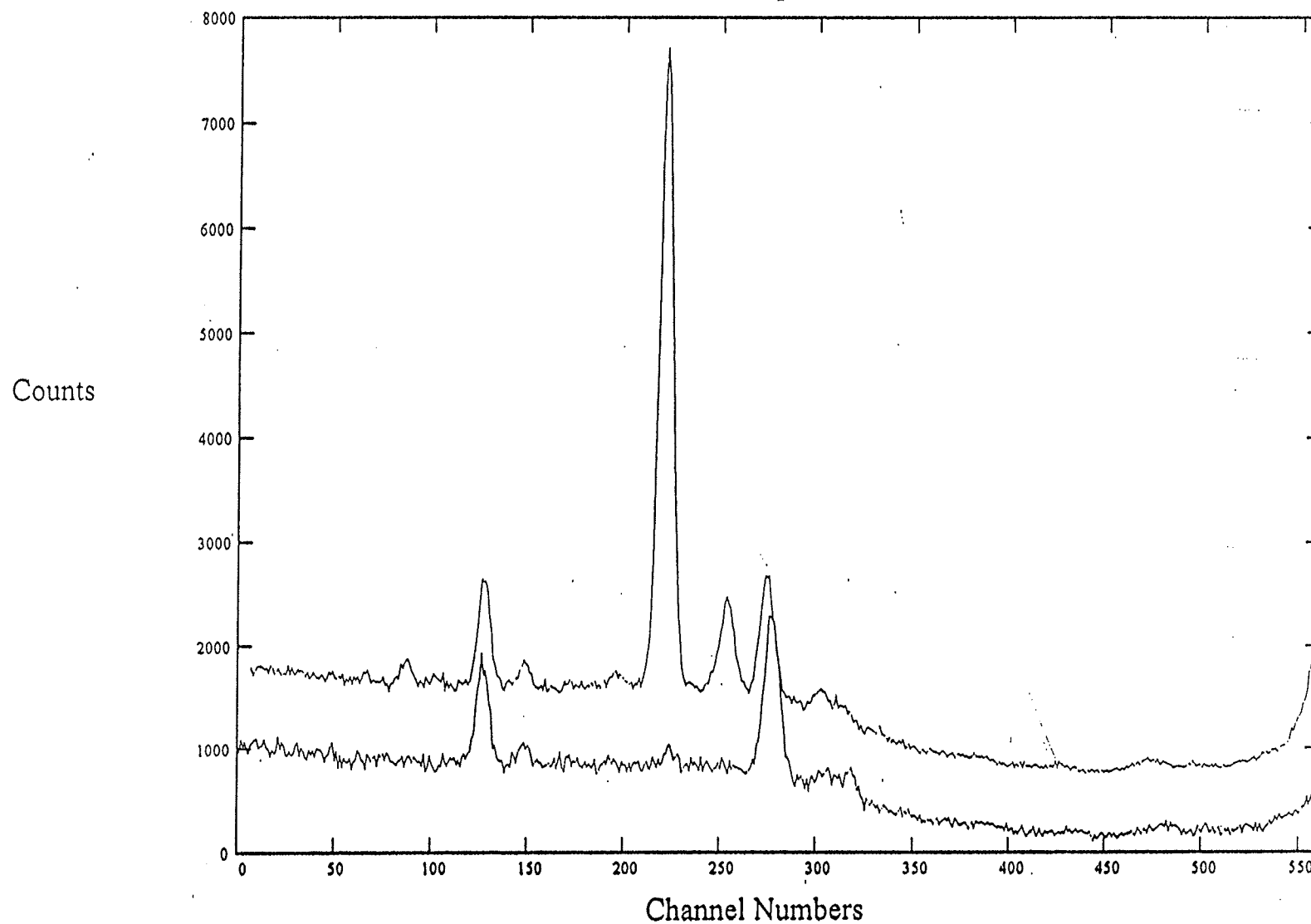
alkali and alkaline earth metals to any great extent.[82,83] In addition, Ca may be sorbed with particulate matter. It was also observed that the peak for Ti after exposure was similar in size compared to the blank recorded previously.

The fact that the monitors were found on the shore of the river after exposure suggests that the metals analyzed may have been present in the sorbed humic material. The amount of free ions in environmental waters has been reported to be only a very small fraction of the total metal content. Such is the case for Cu where only ~ 1 % of environmental Cu is believed not to be bound to organic matter of some sort.[135] This led to the testing of the monitors being deployed which were covered with filter paper.

5.2   ONTARIO TEST LAKE

A second field test of the performance and capabilities of the monitors was carried out in the summer of 1994 in a remote test lake located in northern Ontario. Testing was conducted on the lake with the assistance of personnel from the Department of Fisheries and Oceans who were using the lake as part of a study on the transport phenomena of Cd(II). The lake had been doped with Cd(II) at ~ 200 ng/L.

A total of 12 monitors was given to Dr. D. Malley of The Freshwater Institute, Dept. of Fisheries and Oceans, to be deployed in groups of three at different depths in the lake. The monitors deployed and the depth of deployment are given in Table 10. The time of exposure was 28 days. In order to observe whether or not sorbed organic matter interfered with the analysis, two of the monitors that were used were encased in filter paper (Whatman # 1, qualitative).

After exposure, the monitors were placed in high density polyethylene bags and, due to a shipping error, left for ~ 30 days before analysis. After removal from the bags the monitors were allowed to dry in air before analysis by EDXRF. Spectra were recorded of the monitors before deployment and were used as representative blanks. Spectra of the filter paper were also recorded before and after exposure.

This first set of results, in which a lay-person deployed the monitors, provided several practical points concerning environmental sampling. The first was that a great deal of communication was necessary in order to effect the deployment and eventual return of the monitors. The second point observed was that the sample storage time before analysis was not predictable as in this case where the monitors were misplaced for 1 month.

Table 10. Cloth Used, and Conditions, for Monitors Deployed in the
Test Lake in Northern Ontario.

Sample #	Batch #	Degree of Conversion (%)	Depth of Deployment (meters)	Filter Paper
1	4	70	2	no
2	3	50	2	no
3	6	7	2	no
4	4	70	12	no
5	4	70	12	no
6	6	7	12	no
7	3	50	8	no
8	4	70	8	yes
9	6	7	8	no
10	6	7	5	no
11	4	70	5	no
12	3	50	5	yes

All of the monitors were returned essentially clean, with the exception of the monitors deployed at the 2 metre depth. These were found with algae growing on them. This growth was most likely due to the availability of sunlight, as none of the other monitors experienced this. None of the monitors returned had any detectable soil or clay matter present on them because the lake itself was extremely clean and the water was clear. There was no observable correlation between the monitor used, or the depth of deployment with the resulting metals sorbed. A sample EDXRF spectra recorded one of the monitors after exposure is shown in Figure 38. The peaks of interest are from Fe and Zn.

Observation of the EDXRF spectra recorded on monitors with and without the filters present indicated no discernable difference in the monitors due to the addition of filter paper. There where also no observable amounts of metals present in the filter paper. It was observed, however, that the filter paper used possessed a low mechanical strength as it was found to be torn on both monitors recovered.

Sample λDXRF spectra recorded on the monitors after exposure are shown in Figures 39 and 40. Because of the greater power of the X-ray tube source, the λDXRF instrument proved to be much more sensitive.

Figure 38. EDXRF Spectra Recorded on a Monitor After Deployment in the Test Lake in Northern Ontario.
Peaks correspond to Ti, Fe, Cu, and Zn at 120, 220, 320, and 340 channel numbers respectively.
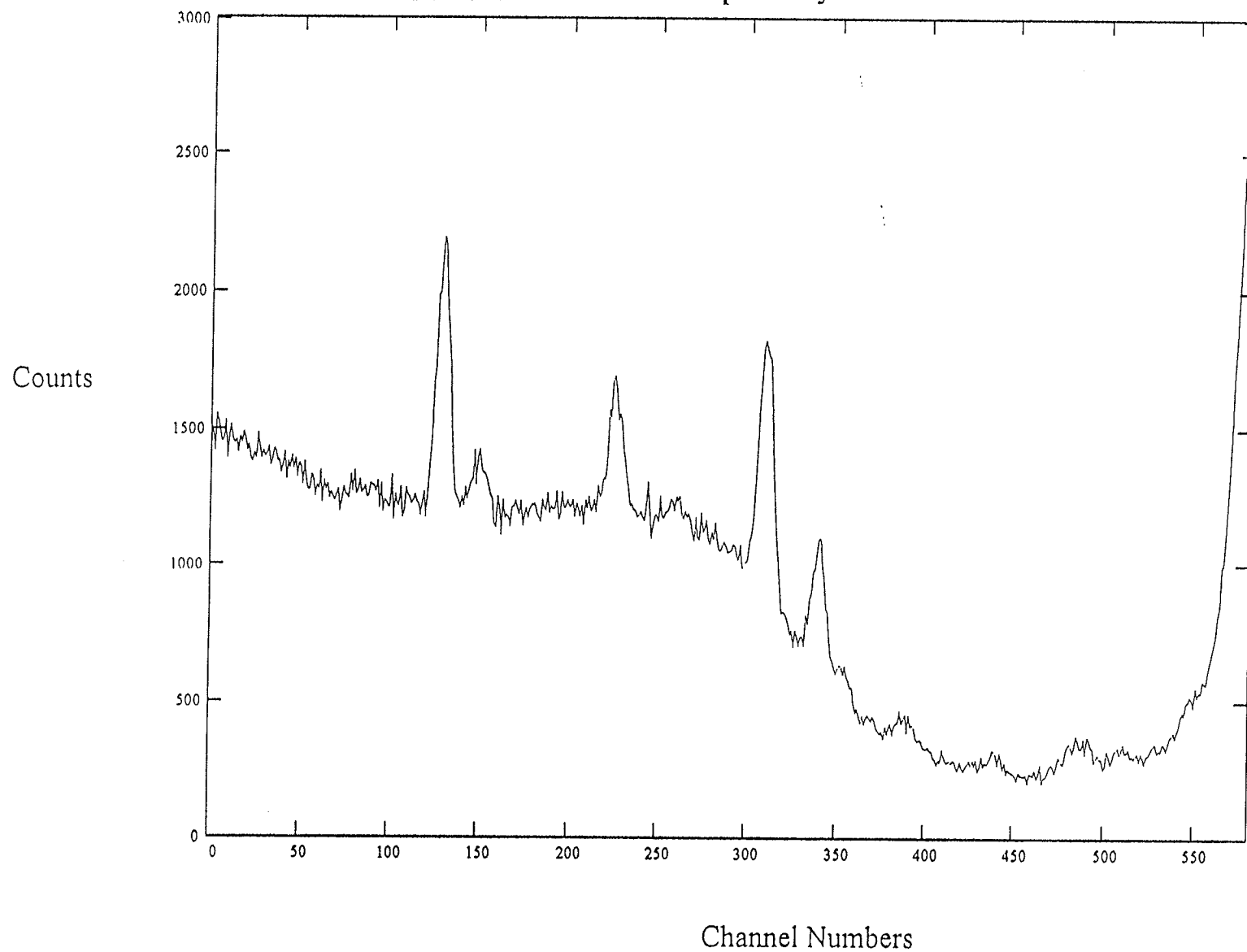
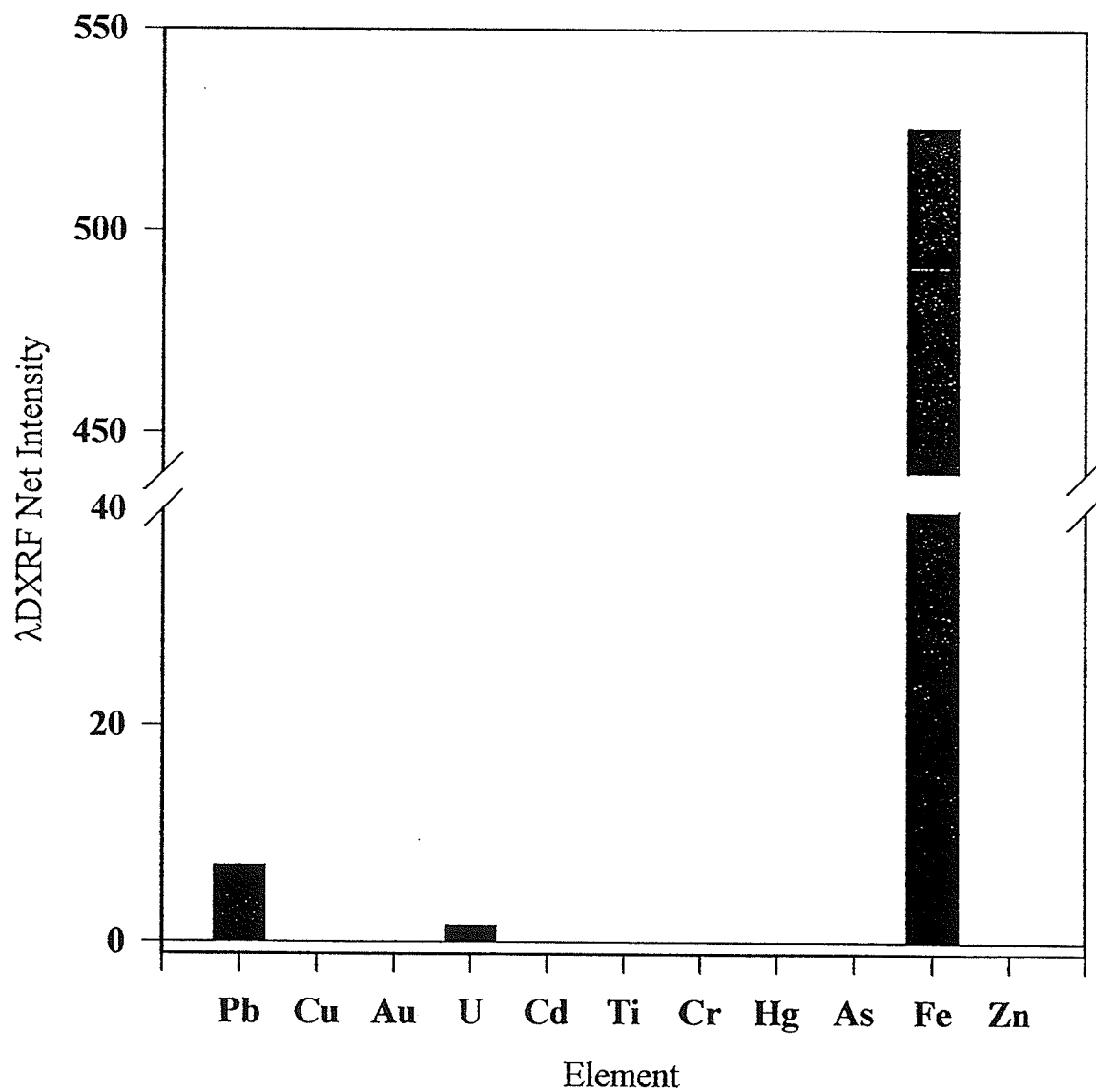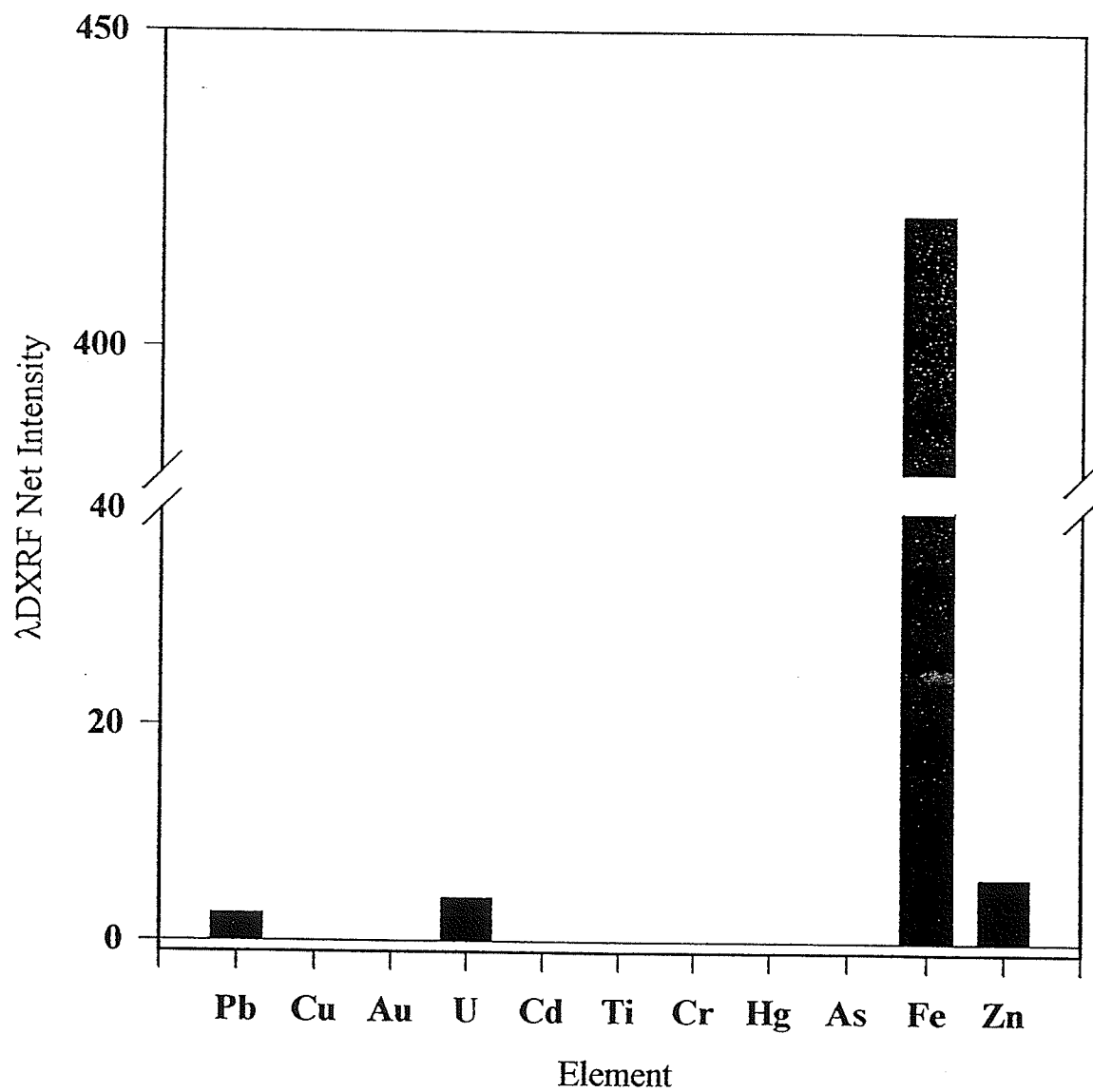Figure 39. Ontario Test Lake, Sample # 6

Figure 40. Ontario Test Lake, Sample # 9

It was observed that both Fe and Zn were present in relatively large amounts. It was also observed that there was a detectable amount of Pb and U present on the cloth as well. The Fe peak is due to the fact that there is a relatively large amount of Fe present in environmental waters. The Pb and U peaks are due to the sensitivity of the λDXRF method for these metals. The absolute amounts of the trace metals present were not calculated, but in the case of Pb, the value was estimated to be in the ng/L range.

As the amounts of the metals analyzed on the cloth were extremely small, it was concluded that the polyethylene bags used for storage and transportation of the monitors had been well chosen. This was due to the fact that there was no detectable amount of sample contamination even though the monitors were exposed to the interior of the polyethylene bags for the same amount of time as the actual deployment time in the lake.

5.3   LaBARRIERE PARK STREAM

A total of three monitors (batch # 26 , 42 % conversion) were deployed in a stream in LaBarriere park, Winnipeg, Manitoba, in May 1995, for a period of 7 days. The water was very clean and clear with a slow to negligible flow rate. Two monitors were attached via monofilament fishing

line to the infrastructure of a bridge which crossed the stream and allowed to simply hang in the water near the centre of the stream. A small piece of glass tubing was tied to each of the monitors and used as a weight. The third monitor was deployed in the centre of the stream by casting it out with a fishing rod and then anchoring the end to the base of the bridge. Again a small piece of glass tubing was used as a weight.

After the time of exposure only the one monitor, which had been cast into the stream, was recovered as the two monitors attached to the bridge had been removed. The recovered monitor was returned to the laboratory for analysis without any surface contact and then allowed to dry in air before being analyzed by λDXRF. A representative blank spectrum was recorded on a piece of clean cloth (batch # 26 , 42 % conversion).

The metals observed on the monitor deployed in LaBarriere park are shown in Figure 41. It was observed that a large amount of Ti was found on this monitor along with a number of other metals in smaller amounts. A number of residential and farm properties were observed border onto the stream and may have accounted for the metals sorbed onto the cloth.

Figure 41. LaBarriere Park Stream
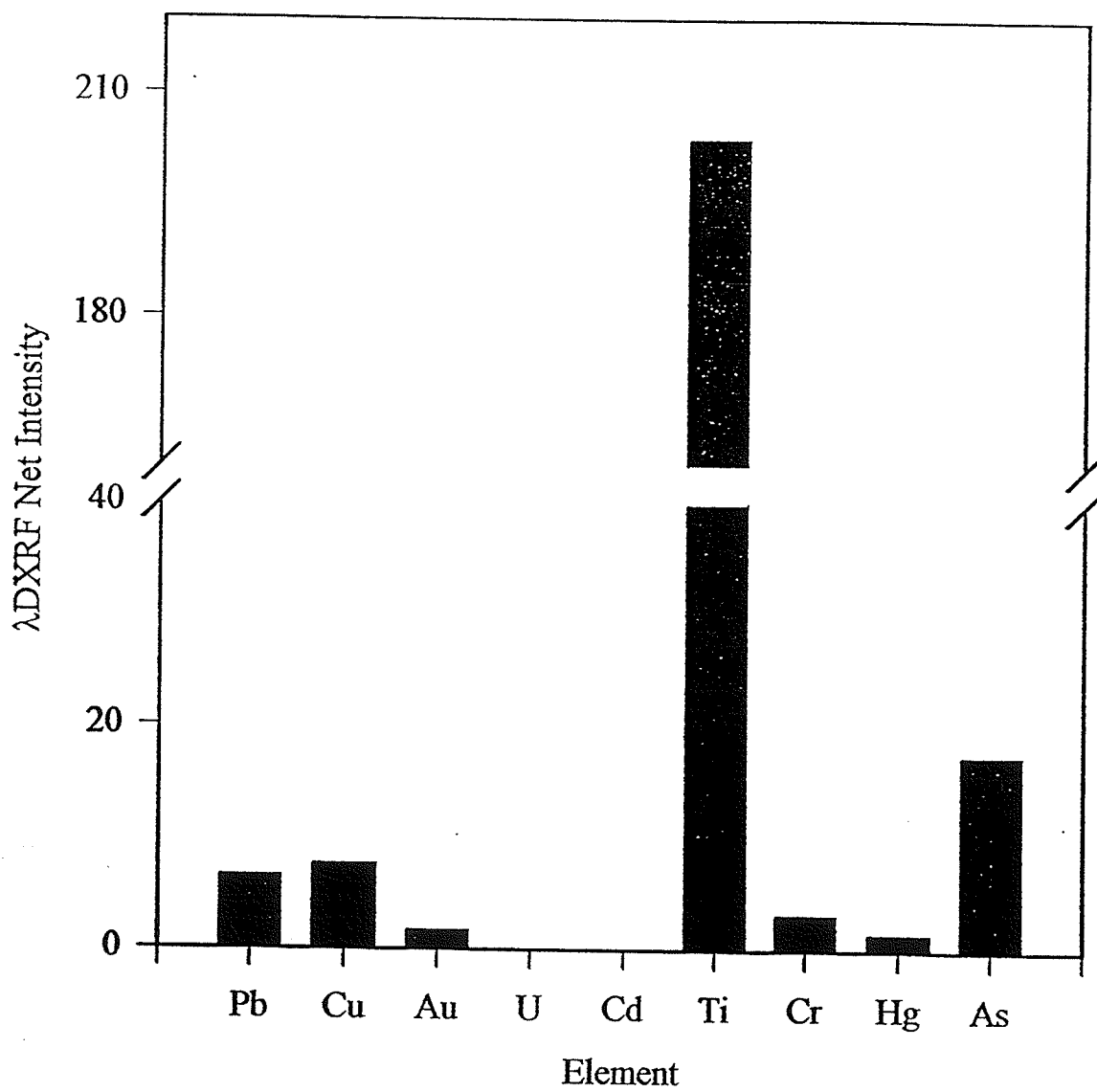
5.4   FLIN FLON MANITOBA

Field testing of a remote river near Flin Flon Manitoba was carried out in order to investigate the feasibility of having a lay-person perform the deployment, collection and return of the passive monitors through the mail. Two monitors were prepared using cloth from batch # 26, 42.4 % conversion. They were placed in polyethylene bags and mailed to Mr. Paul LeBlanc of Manitoba Hydro, Flin Flon, Manitoba, along with instructions on the deployment and return of the monitors. A stamped, self addressed envelope was included to facilitate the return of the monitors. A copy of the instructions can be found in Appendix 8.

As per the enclosed directions, both monitors were deployed in May 1995, in the river which flows near Flin Flon, for a period of 7 days. One of the monitors was deployed before Ross Lake and the other was deployed after Ross Lake. The location of deployment was chosen because the mine in Flin Flon drains into Ross Lake and it was hoped that a change in the amounts of metals sorbed would correspond to the sample location, before and after the water was in contact with the mine run-off. After deployment it was indicated on the accompanying information sheet, that only the one monitor, deployed after Ross lake, was recovered.

The monitor was received, in its polyethylene bag, by mail ~ 7 days after deployment. The monitor was observed to be still wet from the sampling and had some debris on it. The monitor was allowed to dry before analysis with λDXRF. A representative blank spectrum was recorded on a piece of clean cloth (batch # 26 , 42 % conversion). The conditions of monitoring are indicated in the information sheet, which accompanied the monitors, and can be found in Appendix 8.

The total turn-around time, from the date of mailing the monitors to the remote site in Flin Flon MB., the 7 days of deployment, the return trip by mail and the analysis by λDXRF took less than 30 days. This length of time is on par with results of manual grab sampling.[136] The accompanying instructions and sample location questionnaire proved to be useful for the deployment process, although the actual method of sample deployment in which fishing line was used proved to be somewhat inconvenient.[137]

The λDXRF results from the monitor exposed in the river near Flin Flon are given in Figure 42. It was immediately apparent that there was a measurable amount of trace metals present on the monitor. These were presumed to be due to the run-off of the mine being drained into the small lake upstream of the sampling location. It was unfortunate that the monitor

Figure 42. Flin Flon MB.
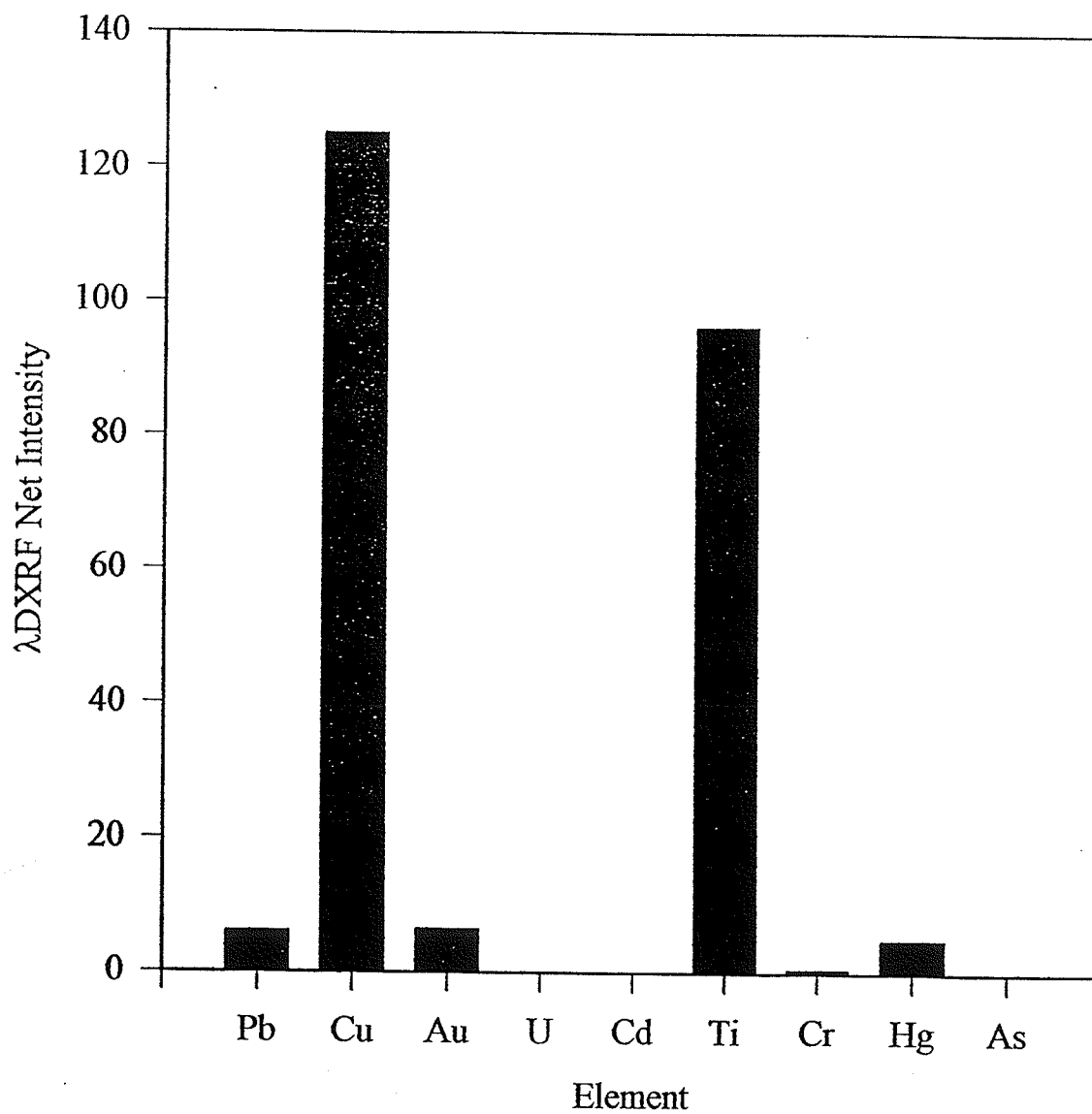
placed upstream of the mine run-off was lost as this would have provided a measure of a representative blank, something which is necessary if point source identification is to be made.

It was also observed that a large amount of Ti was present on the monitor as compared with the blank, results which are similar to those obtained from the sampling at LaBarriere Park. This suggested that the monitor picked up Ti in some form and that the TiO_2 already present in the cloth cannot be used as an internal standard.

5.5   BEAVER CREEK

Investigation of the feasibility of having a lay-person perform the deployment, collection and return of the passive monitors was repeated. As well, the effect of the sorption of particulate matter by the monitors as a source of analyzed metals was examined. A total of 5 monitors were prepared. Three were prepared using cloth from batch # 25, 73 % conversion, one of which was treated in dilute HCl, as described previously, the other two were prepared with plain Orlon cloth. Two of the monitors, one plain cloth and one converted cloth, were encased on either side with a 0.45 μm filter. The monitors were grouped together using monofilament

fishing line and then placed in a polyethylene bag and given to Mr. Richard Oleschuk of The Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, along with instructions on the deployment and return of the monitors.

According to the enclosed directions the monitors were deployed as a group in Beaver Creek, a small stream which flows into the Lee River near Lac Du Bonnet, Manitoba, in June of 1995 for a period of ~ 7 days. After deployment the monitors were recovered, placed in the polyethylene bag and returned for analysis. The monitors when received were observed to be still wet from sampling. Due to instrumental failure, λDXRF analysis of the recovered monitors was not performed. The conditions of monitoring are indicated in the information sheet, which accompanied the monitors, and can be found in Appendix 8.

Although the cloth monitors deployed in Beaver Creek were not analyzed, several useful observations were made. The monitors deployed which used a 0.45 μm filter were found to be entirely particulate free thus indicating the usefulness of the filter. As well, the filter retained its original white color which suggested it was not fouled with organic matter. Thus, use of the 0.45 μm filter was deemed successful in preventing the sorption

of excess particulate matter by the cloth.

Another factor worth mentioning was that the directions indicating the method of deployment were found to be inadequate. This led to the samplers being deployed from a dock at a depth of ~ 15 cm in the water. At such a shallow sampling depth, the monitors may not have been submerged in the water during the entire period of deployment. There existed a greater probability of sample contamination from particulate matter which could fall on the surface of the water. These results indicated that more consideration was needed in the development of the actual deployment of the monitors.

It was also observed that the plain Orlon cloth monitor prepared and deployed retained its original white color and was found to be relatively free from particulate matter. This cleanliness may be attributed to the hydrophobic nature of the polyacrylonitrile fibers of which the cloth is made. In comparison, all of the monitors prepared from the converted cloth, which were not encased in a filter, sorbed a great deal of particulate matter thus indicating a decrease in hydrophobicity.

5.6 RED RIVER FLOODWAY

In order to validate the use of these monitors for the passive sampling of metals, a series of field tests were conducted with the assistance of personnel from Environment Manitoba. Monitors were deployed in the Red River Floodway at two sampling locations used by Manitoba Environment to collect monthly water samples for analysis, as part of the routine analysis of the water near Winnipeg, Manitoba. Locations of monitoring were the Red River Floodway at St. Norbert, Manitoba and Selkirk, Manitoba The use of filter paper to remove particulate matter was further investigated as well.

Two monitors were deployed in May 1995 at the St. Norbert sampling location. The monitors were prepared from cloth derived from batch # 26, 42 % conversion. The monitors were deployed from the bank, one upstream, and one downstream of the floodway gates, for a time of exposure of 7 days. The water conditions were as follows: very dirty and turbid with a fast rate of flow.

After exposure, only the monitor deployed upstream of the gates was recovered and the other monitor was presumed to have been lost. The monitor was placed in a polyethylene bag for ~ 30 minutes during

transportation to the laboratory. The monitor was allowed to dry in air before analysis with λDXRF. The monitor was observed to be covered in fine particulate matter from the turbid river as well as some organic matter.

For the second sampling location, a total of 4 monitors were prepared (cloth batch # 31, 52 % conversion), two of which were encased on either side with a 0.45 μm filter. The monitors were deployed at Selkirk, Manitoba from a concrete infrastructure on the shore of the river, ~ 1/2 km upstream of the site of grab sampling, for a time of exposure of 7 days.

After exposure the monitors were placed in polyethylene bags for ~ 2 hours while they were transported to the laboratory. Again, due to instrumental failure, λDXRF analysis of the recovered monitors was not performed. Water conditions were the same as those observed at St. Norbert. The monitors which did not have the 0.45 μm filter were observed to be covered in fine particulate matter from the turbid river. The filter paper on one of the encased monitors was torn thus allowing the cloth surface to become covered in particulate matter. The filter paper on the remaining covered monitor was intact. The filter was observed not to retain any particulate matter compared with the bare cloth monitors deployed.

By working in conjunction with Environment Manitoba, an attempt was made to try and provide a degree of correlation with respect to the amounts of metals observed on the monitors and the amounts of metals analyzed from direct grab samples. A summary of the metals analyzed by Environment Manitoba and their respective amounts is given in Table 11. It was found that the majority of trace metals which were targeted for this research were found at levels below the minimum detectable amount. Because of this it was difficult to ascertain the degree of correlation compared with the results obtained from the analysis of the monitors.

The λDXRF results recorded on the monitor recovered from the St. Norbert sampling location are shown in Figure 43. As with the previous spectra, a number of metals were observed to be present on the cloth in trace amounts. However, it was not possible to provide any degree of correlation of these results with the results from the aqueous grab samples due to the low concentrations of metals observed. However, it can be stated that the method of analysis presented here is more sensitive than the typical standard method used by Manitoba Environment, which involves ICP and GFAA as the means of analysis.

Table 11. Concentrations of Metals Found in the Red River Floodway for the Month of June, 1995.[136]

Metal	St. Norbert MB.	Selkirk MB.
	Concentration mg/ Litre	Concentration mg/ Litre
Na	42.6	38.1
K	8.0	8.7
Ca	88.1	72.7
Mg	43.1	35.5
Zn	0.03	0.02
Cu	0.01	<0.01
Fe	3.77	2.41
Mn	0.67	0.29
Ni	0.007	0.006
Cd	<0.001	<0.001
Pb	0.0020	0.0020

1) Sampling conditions: ~500 mL grab sample, filtered 0.45 μm, 2.5 % in HNO_3 as preservative.

2) St Norbert MB. : Turbidity = >200 NTU, Conductance = 822 Ω^{-1}
   Selkirk MB. : Turbidity = 120 NTU, Conductance = 735 Ω^{-1}

Figure 43. Red River Floodway, St. Norbert, MB.
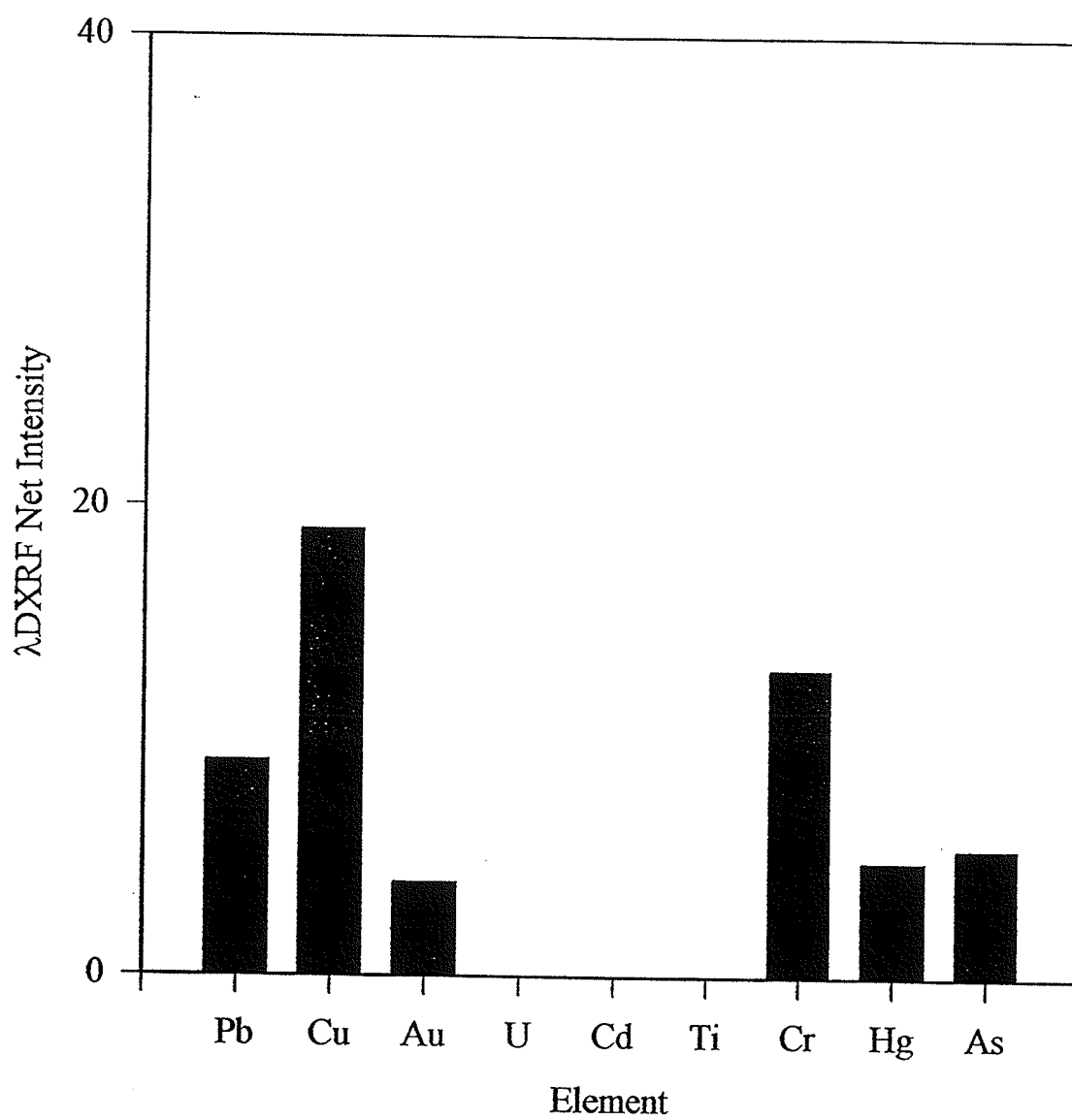
Due to equipment failure, the analysis of the monitors deployed at Selkirk, Manitoba by λDXRF was not possible during the closing phase of this research. However, the experiment was not without results. Visual observation of one of the filter covered monitors indicated that the filter was successful in preventing the sorption of particulate matter of sizes > 0.45 μm by the cloth. The filter retained its original white color and the cloth was observed to be completely free from particulate matter after the removal of the filter. It was observed that with the other filter-covered monitor, that the filter had torn during the time of sampling. This was presumed to be due to the fast flow rate of water at the sample location as well as the lack of strength in the filter.

5.7   SUMMARY

In summary the limited field tests were successful in demonstrating the feasibility of using the chelating Orlon cloth as a passive monitor for trace metals in water. As well, some the potential difficulties that might be encountered were identified.

CONCLUSIONS

From the results of this research a number of conclusions can be made with respect to the preparation and use of polyacryloamidoxime cloth as a passive monitor for trace metals in water.

The preparation of the cloth and the subsequent monitors proved to be relatively easy, controllable and cost effective. The following conditions were deemed optimum for the conversion process: concentration of $NH_2OH*HCl$ = 2.0 % (m/v) in 50 % (v/v) methanol/water, pH = 7, temperature = 55 °C for 12 hours. The final process used had a reproducibility of ~2 % and can be adapted to a commercial scale. The cloth produced at ~ 45 % conversion has good physical properties with respect to strength and a relatively large capacity for metals of 1.12 and 2.17 mmol/ gram for Cu and Pb respectively.

Processing the cloth with HCl resulted in a slight improvement in the amount of metals taken up but at the same time caused the cloth to swell and then contract which produced a cloth with poorer physical properties. Treatment with NaOH or NH_4OH was also found to degrade the physical properties of the cloth without providing any real benefit.

The physical nature of the monitor suggests an indefinite storage time when dry. The actual size of the monitors was ideal for both EDXRF and λDXRF analysis as well as for acid extraction followed by AA or GFAA analysis. In addition the size of the monitors was convenient for delivery by mail.

The choice of amidoxime as a ligand was acceptable and proved to be selective to metals of interest and not the alkali and alkaline earth metals. The kinetics of metal sorption, capacities and distribution coefficients, for Cu and Pb were similar to that of resins and fibres which contained amidoxime groups.

From the *in vitro* experiments the effect of different variables as experienced in the environment such as the rate of flow, the temperature of the water and the effect of turbulence on the kinetics of metal uptake were explained. The *in vitro* experiments demonstrated the sensitivity of this method with Kd values in the 10^6 range for Cu and Pb. The precision of the method was observed to be better than 10 %. Use of a particulate-bound metal imbedded within the fibres, such as TiO_2, was found to be a better internal standard compared with a surface chelate-bound metal such as Au.

The use of EDXRF proved to be a sensitive and relatively easy

method of analysis. The multi-element capability was advantageous as it allowed for the simultaneous screening of all elements in question. The λDXRF instrumentation proved to be more difficult to use, costly and prone to failure, but possessed a sensitivity several orders of magnitude greater than the EDXRF instrument.

The limited field tests demonstrated the relative ease of deployment of the monitors even by untrained personnel. Although only one attempt was made using a mailing program, it was demonstrated to be as feasible as in the case of the passive air monitors developed in this laboratory.[59] Concentrations of metals in the environment were observed at levels lower than those typically measured thus indicating the sensitivity of the method and the ability of the cloth to concentrate the trace metals. The use of a filter was successful in preventing the excessive contamination of the monitors with particulate matter.

In summary, the passive sampling and monitoring of trace metals in environmental waters such as rivers and lakes is feasible. With these monitors both qualitative and semi-quantitative results may be obtained at present. The cloth monitors are directly applicable for monitoring processes, point and non-point pollutant source identification and the study of transport

phenomena. The deployment of the monitors and their subsequent analysis was proven to be simple, straightforward, and relatively inexpensive.

SUGGESTIONS FOR FUTURE WORK

There are a number of different avenues of exploration available stemming from this work.

Investigation into other reaction conditions concerning the conversion of the Orlon cloth to the polyacryloamidoxime chelating cloth may be carried out. Use of different types of Orlon cloth, and fibre precursors, should be looked at with the goal of increasing the surface density of chelating groups and maintaining the accessability of bulk sites. The use of copolymers with the amidoxime groups may be investigated with the goal of increasing the hydrophillicity of the cloth. The manufacture of a monitor with a round shape in a suitable frame would allow easier direct analysis by λDXRF.

An increase in the hydrophillic nature of the cloth monitor, by means of a copolymer, different chelating groups, or modification of the amidoxime group may result in an increase in the kinetics of sorption. Different chelating groups may be investigated as it was observed that the amidoxime group had a strong affinity for Fe which may, in some cases, be considered a matrix element. It would be advisable to try a chelating group which forms a multidentate 1:1 complex with all the metals in question rather than

1:2 or 1:3 complexes, in manner similar to that of pendant complexes.

Continuation of the *in vitro* experiments should be carried out with more metals of varying charges in solution in order to ascertain any correlation with the types and amounts of metal in solution, their relative rates of sorption and their respective K_d coefficients. The net result would be an attempt to develop a model which would simplify the process involved in applying the monitors in a quantitative manner.

The nature of the sorption of Cu at varying concentrations of Pb should be investigated to better understand the sorption processes involved. Also the rate of Cu desorption should be investigated to determine if the formation of a multiple chelate complex has any effect on the rate of desorption. *In vitro* experiments should be carried out with the 0.45 μm filter in order to observe the effect of the filter on the sorption of metals. Different materials such as fibreglass should be investigated as filter material. The use of a different metal as an internal standard should also be investigated, perhaps one that would not be expected in the environment. The effect of an initial washing period on the use of a particulate bound internal standard such as TiO_2 should be investigated.

The use of field testing ought to be further explored. Improvements in the method of deployment and handling of the monitors should be looked at in order to develop a routine and foolproof method. Comparative studies could be performed with active sampling under a variety of conditions in order to draw a correlation between the two methods..

The use of different instrumentation should also be investigated. Use of tube source EDXRF or total reflection X-ray fluorescence as the method of analysis may result in an increase in the speed and sensitivity of analysis. It is also possible to extract the metals from the cloth followed by subsequent analysis with ICP, AA or by GFAA. A comparison of the different possible methods of analysis of the cloth monitors should be done.

It is possible, with only a moderate amount of further research, to develop this methodology to the point of producing a passive monitor which will allow for qualitative and quantitative analysis of trace metals in environmental waters.

Appendix 1.   Q-BASIC Program for Spectral Analysis

The following program is a modification of the program originally written by Dr. L.J. Kruczynski of the Dept. Of Chemistry, University of Manitoba. The program converts a spectrum recorded with the EDXRF instrument into a format which can be recognized by Mathcad. This allows the evaluation and plotting of spectra.

```
DIM scr(640)
DIM cr%(600)
DIM bytea(2000) AS LONG
DIM byteb(2000) AS LONG
CLS
PRINT
PRINT
PRINT
PRINT "This Program Will Convert an XRF File to Mathcad format"
PRINT "The File Must be in the following directory.."
PRINT "'d:\mark\xrf\markfile\new'"
PRINT
PRINT
INPUT "enter filename:   ", filenm$
disknm$ = "d:\mark\xrf\markfile\new\" + filenm$ + ".chn"
OPEN disknm$ FOR BINARY AS #1
hdr$ = INPUT$(32, #1)
badch$ = INPUT$(400, #1)
REM ymin = 0: ymax = 0
FOR i = 1 TO 1900

   a$ = INPUT$(2, #1)
   b$ = INPUT$(2, #1)
   bytea(i) = CVI(a$)
   byteb(i) = CVI(b$)

IF byteb(i) = 0 THEN
      : IF bytea(i) > 0 THEN bytea(i) = bytea(i)
      : IF bytea(i) < 0 THEN bytea(i) = bytea(i) + 32768 + 32768
```

```
ELSE

REM IF byteb(i) = 1 THEN
        : IF bytea(i) > 0 THEN bytea(i) = bytea(i) + 32768 + 32768
        : IF bytea(i) < 0 THEN bytea(i) = (4 * (32768)) + bytea(i)
END IF

NEXT i
  CLOSE #1
  outnm$ = "d:\mark\xrf\markfile\mcad_xrf\" + filenm$ + ".dat"
  OPEN outnm$ FOR OUTPUT AS #2
  FOR j = 1 TO 1900

  WRITE #2, bytea(j)

  NEXT j
  CLOSE #2
500    END
```
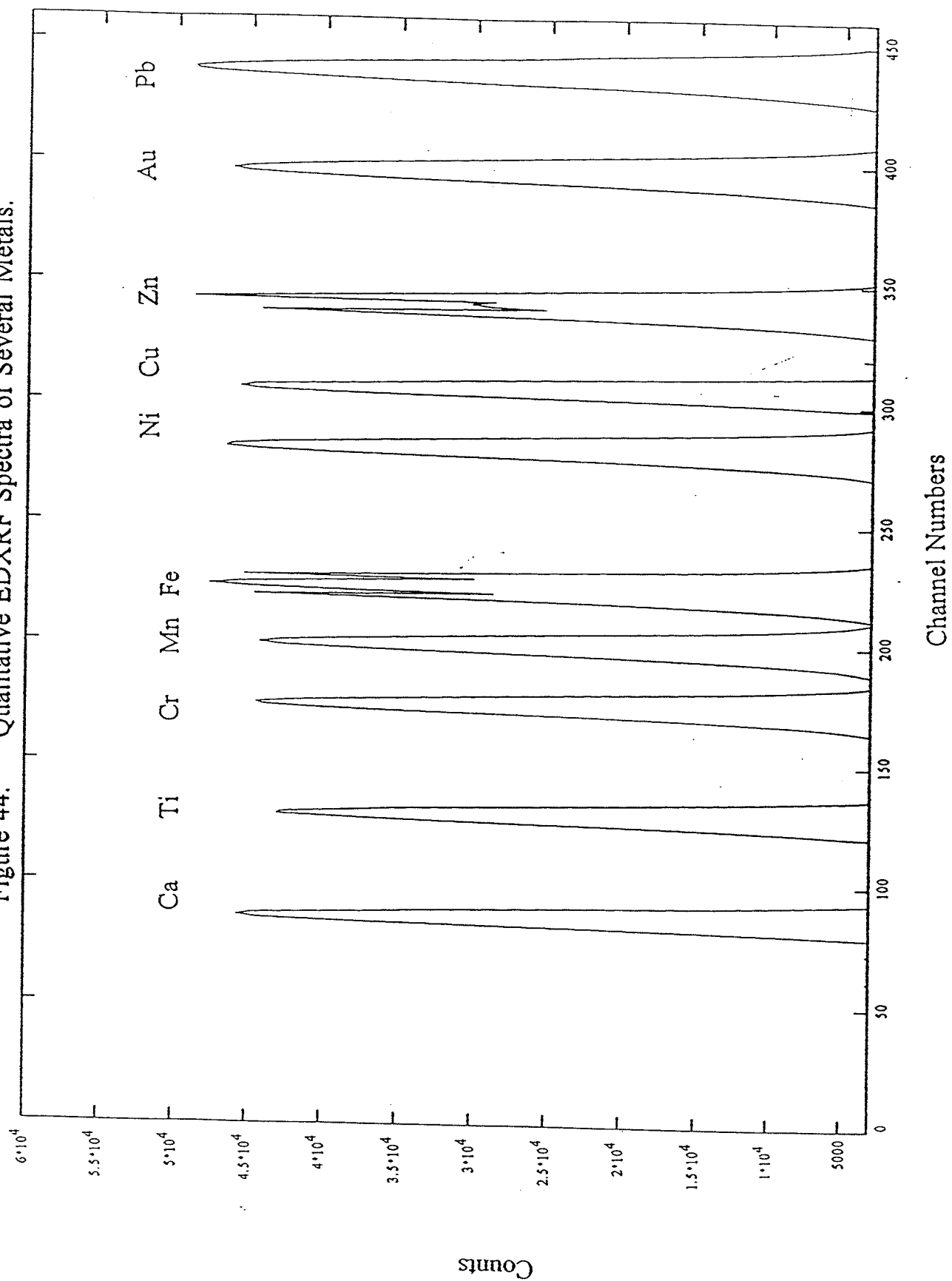
Appendix 2

Figure 44.   Qualitative EDXRF Spectra of Several Metals.

Counts vs Channel Numbers — spectra labelled Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Au, Pb

Appendix 3

Table 12.   Operating Parameters of the λDXRF Spectrometer.

Element	Line	Count time (seconds)	2 Theta (Real) (degrees)
Ti	Kα11	20.0	86.1400
Cr	Kα11	20.0	69.4200
Fe	Kα11	20.0	57.5300
Cu	Kα13	30.0	45.0500
Zn	Kα13	20.0	41.8000
As	Kα13	30.0	30.4800
Cd	Kα13	30.0	15.3100
Au	Lα13	30.0	36.8800
Hg	Lβ13	30.0	30.1900
Pb	Lβ13	30.0	28.2600
U	Lα13	20.0	26.1400

Appendix 4.

Figure 45. Calibration Curves Relating λDXRF Intensities and

EDXRF Net Peak Areas for Cu and Pb
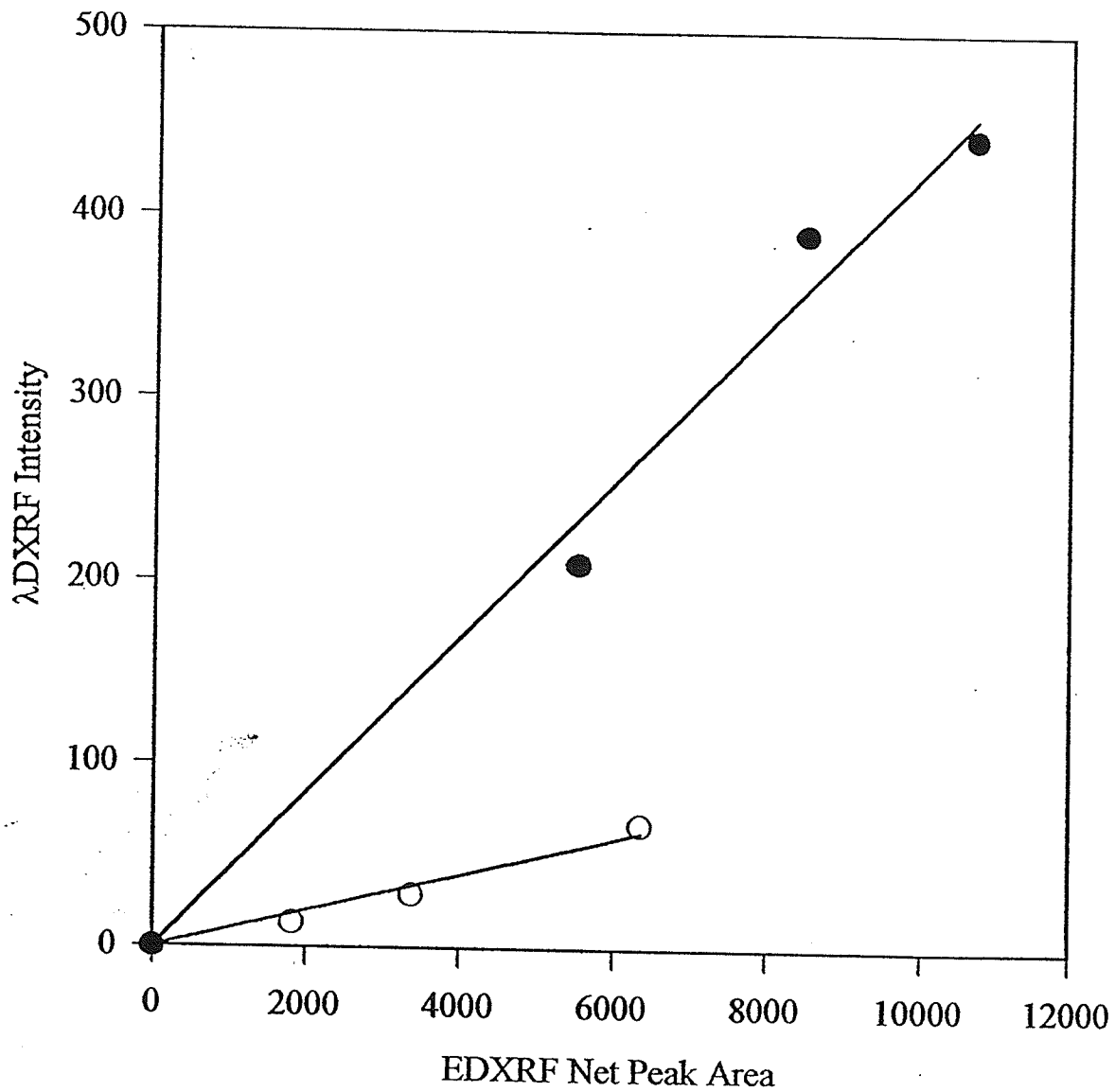
R^2 Cu = 0.993, R^2 Pb = 0.992

Appendix 4.

Figure 46.   Calibration Curves Relating EDXRF Net Area With Molar
Amount of Pb and Cu.
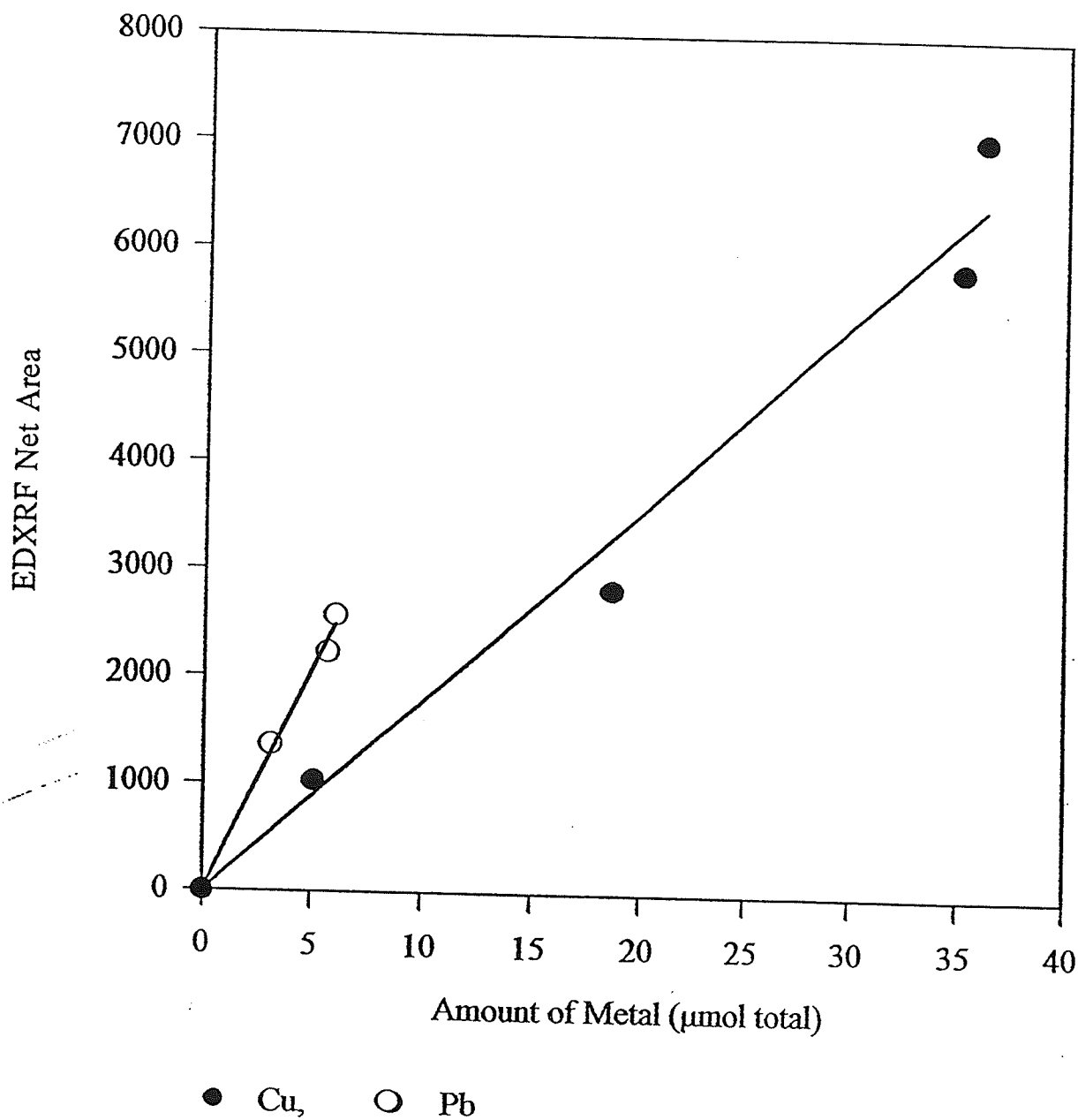
R^2 Cu = 0.989, R^2 Pb = 0.996

Appendix 5.

Table 13. Degree of Extraction on a Sample of Cloth

# Extracts	Amount extracted (μgrams)		Amount extracted (μmoles)		Degree of extraction (%)[1]	
	Cu	Pb	Cu	Pb	Cu	Pb
1	215	125	3.4	.60	89	98
2	23	1.8	.36	.01	9	2
3	4.1	.42	.06	0	2	0
Total	242	127	3.82	.61	100	100

1)   The degree of extraction was calculated assuming that the total amount of metal extracted after three extraction was quantitaitve.

Appendix 6

Table 14. Properties of the Polyacrylonitrile Cloth Used

Material	Properties
Orlon Cloth Manufactured by Test fabrics Inc. P.O. Box 420 Middlesex NJ USA, 08846	Orlon Type 75 100 % Acrylic style # 864 lot # 8400
Orlon Fibres Manufactured by Dupont Canada Inc. P.O. Box 2100 Kingston, Ont. Canada, K7L 4Z6	Spun Orlon, Type 75 Dupont yarn, acrylic yarn 30/2 warp - 44 end/inch 30/2 warp - 40 pick/inch 30/2 = 19.68 Tex x 2 ply yarn

Appendix 7.

Table 15.   Properties of Polyacrylonitrile Fibres[129,130]

Physical Property	
Degree of polymerisation	~ 2000
Average density	1.16 g/ cm^3
Crystallinity	~70 - 80 % crystalline
Tenacity	20 - 23.5 g/tex (wet - dry)
Plastic	2 - 10 % elongation
Elastic	97 - 72 % elastic recovery
Hydrophillicity	Very hydrophobic
Moisture regain	~4 % at 100 % RH
Heat Sensitive	Softens 235 °C Decomposes 280 - 330 °C
Fibre length	~10 - 150 mm
Fibre diameter	~15 - 25 um
Polymer length	~500 nm
Polymer diameter	0.3 nm at methylene 0.53 nm at CN
Inter-polymer forces	Van der Waals' ~8 - 10 kJoules
Inter-polymer distance	0.2 nm
Reactivity	Saponification with NaOH $C{\equiv}N + NaOH \rightarrow COO^-Na^+ + NH_4OH$
TiO$_2$ added	Up to 2 % (w/w) to pre-polymer Irregular particles < 1.0 μm

Appendix 8.

INSTRUCTIONS FOR PASSIVE WATER MONITORS

1. Take slide out of plastic bag and try not to touch the cloth centre. Save the bag.

2. Attach the slide to enough fishing line to ensure that it will reach the water to be tested.

3. Secure one end to a suitable anchor and throw the slide into the water.

4. Record the time and date of deployment. Record the water conditions below.

5. After a suitable length of time remove the slide from the water. Try not to touch the cloth centre. Record the time and date.

6. (Optional) If possible let the slide dry overnight.

7. Cut off the fishing line and place the monitor inside the plastic bag.

8. Mail the monitor in the enclosed envelope.

Location of testing: _____

Time and date of deployment:_____

Time and date of recovery: _____

Name:_____

Address:_____

Phone #:_____

Check all that apply

Conditions of water:	☐Clear	☐Murky	☐Muddy
Location:	☐Lake	☐River	☐Well
Flow rate:	☐Fast	☐Slow	
Bank conditions:	☐Mud	☐Rock	☐Gravel
Distance from shore:	_____feet.		

If you have any questions contact: Mark McComb, (204)-474-9893
Dept. of Chemistry, University of Manitoba. WPG. MB.   R3T 2N2

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5. After a suitable length of time remove the slide from the water. Try not to touch the cloth centre. Record the time and date.

6. (Optional) If possible let the slide dry overnight.

7. Cut off the fishing line and place the monitor inside the plastic bag.

8. Mail the monitor in the enclosed envelope.

Location of testing: _____ AFTER ROSS LK. _____ (B) _____
Time and date of deployment: _____ MAY 03-1995 _____ 10.30 AM
Time and date of recovery: _____ MAY 10-1995 _____ 10.30 AM

Name: _____
Address: _____
Phone #: _____

Check all that apply
Conditions of water: ☑Clear   ☐Murky   ☐Muddy
Location: ☐Lake   ☑River   ☐Well
Flow rate: ☐Fast   ☑Slow
Bank conditions: ☑Mud   ☐Rock   ☐Gravel
Distance from shore: _____ 5 _____ feet.

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INSTRUCTIONS FOR PASSIVE WATER MONITORS

1. Take slide out of plastic bag and try not to touch the cloth centre. Save the bag.

2. Attach the slide to enough fishing line to ensure that it will reach the water to be tested.

3. Secure one end to a suitable anchor and throw the slide into the water.

4. Record the time and date of deployment. Record the water conditions below.

5. After a suitable length of time remove the slide from the water. Try not to touch the cloth centre. Record the time and date.

6. (Optional) If possible let the slide dry overnight.

7. Cut off the fishing line and place the monitor inside the plastic bag.

8. Mail the monitor in the enclosed envelope.

Sample # : _____

Location of testing: _Beaver Creek_____

Time and date of deployment: _Jun 25th/95_____

Time and date of recovery: _July 3/95_____

Name: _Richard Oleschuk_____

Address: _323 Highcliff Bay_____

Phone #: _632-0290_____

Check all that apply

Conditions of water:	☐Clear	☒Murky	☐Muddy
Location:	☐Lake	☒River	☐Well
Flow rate:	☐Fast	☐Slow	☒ Medium
Bank conditions:	☒Mud	☐Rock	☐Gravel
Distance from shore:	_12_ feet.		

If you have any questions contact: Mark McComb, (204)-474-9893
Dept. of Chemistry, University of Manitoba. WPG. MB.   R3T 2N2

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