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A NEW PRECONCENTRATION TECHNIQUE FOR ULTRA-TRACE METAL DETERMINATION IN FRESH WATER

by

XIN-QIANG ZHOU, M. Eng.

A thesis submitted to the Faculty of
Graduate Studies and Research
in partial fulfilment of the
requirements for the degree of
Master of Science

Department of Chemistry

Carleton University
Ottawa, Ontario
May, 1993

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**A NEW PRECONCENTRATION TECHNIQUE FOR ULTRA-TRACE
METAL DETERMINATION IN FRESH WATER**

Submitted by XIN-QIANG ZHOU, M. Eng.

in partial fulfilment of the requirements for
the degree of Master of Science

Thesis Supervisor

Chair, Department of Chemistry

Carleton University

May, 1993

ABSTRACT

Various filter media which were potentially used for an Automatic Preconcentration Sampler (APS) have been studied to assess their relative efficiencies in trapping dilute metals from fresh water. Through comparison of their capacities, Celite was selected as the most effective filter medium with which to prepare a three dimension depth filter for preconcentration and analytical purposes because of its high-surface-particle trapping capacity. Optimization test with the Celite as filter medium has been carried out in order to pass turbid water with large sample volume in high flow rate.

The different precoated Celite with various metal hydroxide in the filter was used as the filter media for APS system to trap trace heavy metals from fresh water. The efficiencies of the trapping were compared at various conditions. At optimum condition, aluminum hydroxide precoated celite appeared as the best trapping material. With aluminum hydroxide precoated Celite as the filter medium, the percentages of total metals in water trapped in the filter were 30% to 90% for As, Hg, Cd, Cu, Cr and Pb respectively. The good recovery rates for most of the above metals were obtained with spiked river water at ppt level by using the APS system.

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A. INTRODUCTION

A.1 Current Techniques of Trace Water Analysis

The qualities of natural water are of immense concern from the standpoint of both human health and the condition of environment. Within the environment, water is one of the most important media for transport and redistribution of pollutants. The concentration of pollutants in natural water also determines the levels appearing in life forms living in the medium or using water for drinking. Thus, regulatory bodies around the world are setting increasingly stringent limits on the maximum acceptable concentration levels (MACL) for pollutants in water sources, waste water streams and sewage systems. This trend has placed increasing requirements on chemical analysis capabilities. At present, detection limits in part per billion (ppb) or part per trillion (ppt) are mandated for many organic contaminants and several heavy metals in drinking water or in waste water being reintroduced to the environment. In future these limits will likely be reduced even further.

As the severity of detection limits is increased in this

way, all aspects of the accuracy, precision and convenience of conventional analytical procedures become stressed to their limits of reliability. Usually, analysis consists of three distinct steps, sampling, isolation and detection. In each step, the ultimate ability to quantitate a trace level contaminant is limited by characteristic problems which are difficult to overcome.

In the sampling step, traditional procedures employ grab sampling in 1L vessels. The two main problems are the size of the sample and the potential for contamination. Depending on the type of detection available, the mass of the contaminants in these samples may be insufficient for quantitation. At the same time, any contamination of the vessel during handling, filling or storage can obscure the presence of the pollutant of interest during quantitation. This is minimized by cleaning and careful handling but as detection limits are lowered, the material of the vessel itself can leach into the sample water. As well, vigorous cleaning tends to activate vessel surfaces which then physically or even chemically adsorb the pollutant from the water. This lowers the apparent pollution concentration unless corrective action is taken.

In the isolation steps, both sample loss and contamination are encountered again. The pollutants of interest can be lost at any point during its extraction from the original water sample. Loss can occur onto surfaces, by incomplete separation from the aqueous into non aqueous extraction solvents, by volatilization during solvent reduction or by retention on chromatography columns. At the same time, the pollutant sample can be contaminated by materials leached from any solid materials or present in solvents used during isolation.

In the detection step, the pollutant is usually prepared as a 1mL solution. From this only 1uL is used for the actual quantitation step for most detectors. This means that three orders of magnitude of sample loss occur as a result of conventional practice during the detection procedure. Often attempts are made to compensate for this loss by increasing the sensitivity of the detectors. This is usually a self-limiting approach and it is rare that a compensation of 1000 times can be achieved. Only the most highly developed GC/MS/MS for organic pollutants and ICP/MS for inorganic pollutants achieve this compensation.

Sample contamination often interferes with detection of target pollutants. The organic leachates from surfaces or contaminants in solvents often resemble organic pollutant compounds quite closely. They may be difficult to separate chromatographically and may have very similar mass spectrometric patterns. Similarly, spectroscopic backgrounds from contaminant inorganic substances can interfere with detection of target metal ions.

Beyond all these procedural limitations, traditional trace pollutant analysis is, by its conception, a batch process. As a result, it is difficult to adapt this form of trace analysis to continuous processes such as drinking water or sewage treatment systems. Present continuous monitoring devices, such as ion selective electrodes, suffer two disadvantages. One is poor sensitivity and the other is susceptibility to fouling. These problems mean that such devices cannot be used for trace analysis and require significant maintenance.

To overcome the problems of both the batch trace analysis and the continuous high concentration analysis system, a semi continuous system based on preconcentration is a potential

option. In these systems, sample water is pumped through a medium which concentrates the sample before quantitation. This strategy provides several potential types of freedom in optimizing conditions for trace analysis. The first is that the ultimate detection level may be reduced to any desired level by sampling from a sufficiently large volume of water. The second is that, even when very low detection levels are not needed, preconcentration can collect sufficient material for quantitation by less sensitive but more convenient detectors. The third is that collection of a concentrated sample in a small clean sealed chamber permits simple handling with high protection against contamination. The fourth is that the volume reduction achieved at the collection site reduces substantially the number of steps needed for isolation.

However, to take full advantage of all these potential benefits, the trapping medium must meet several stringent criteria. It must permit rapid and continuous flow of water without blocking up during sampling of the desired water volume. At the same time it must trap the target pollutants with high efficiency at part per trillion levels. Indeed this

must happen even if the pollutants occur in typical fresh water samples containing suspended solids. These two requirements are essentially contradictory when conventional trapping concepts are applied. Normally those solid media capable of trapping trace levels are rapidly blocked by suspended solids, especially from large volumes of water.

One approach toward overcoming these limitations is an on-site preconcentration device which is based on the removal of the soluble analytes from water by beaded sorbents packed in a column^(3,4) through which the water sample is passed. However, the capture of the particulate phase from the water stream by analytical filtration is usually also required in this process. Then the trapped analytes must be extracted from both the filter and the column for quantitation.⁽⁶⁾ In 1985, the Ontario Ministry of Environment, Health and Welfare Canada and Carleton University in Ottawa began investigating techniques to improve these preconcentration methods for dioxins in water sources at low concentration levels. The net result of this effort was the development of two prototypes of the Mark II APS system, one for preconcentration of organics and the other for the preconcentration of heavy metals⁽⁵⁾.

In these preconcentration systems, the target metals in the waste-water or fresh water are either trapped in the filter in the particulate form or adsorbed on the surface of the ligand-attached resin column as immobilized species. The major limitations of these preconcentration samplers are the inefficiencies of commercial filtering media and low sample volume capacities in both filters and resins. As a result, the first available preconcentration systems had very large filtration devices using either two dimensional sieve filters or three dimensional depth filters, both of which can be contaminated during manufacture. In spite of many attempts to maximize filter capacity, most filters were found to be inadequate for sampling high NTU (Turbidity Units) raw water at the high flow rates which are required for efficient on-site, real-time sampling.

The alternative to both filtration and surface adsorption is chemisorption. However, the normal immobilized trapping compounds⁽⁵⁾ are apt to bleed from the resin during the sampling process because of the high or low pH of sampled water. Moreover, in the neutral pH of most fresh water sources, most of heavy metals ions are present as hydrolysed particulates⁽⁶⁾

rather than soluble ions. Consequently, the major requirement in trapping trace metals is for an effective analytical trapping medium for capturing of these metal particulates. On the other hand, if the dissolved metal species could also be trapped effectively in the same analytical trapping medium, then the need for the unstable ligand-attached resin column could be eliminated at same time. Furthermore, the trapping conditions such as pH might be manipulated to trap either just the metal particulates or both the metal particulates and the dissolved metal species. As a result, the distribution of metals between these two species could be known.

In summary, the prospective chemisorption trapping system for pollutant metals would involve the following desirable capabilities:

- 1). Immobilization of the target metal ions from large volume of water at or below the ppb concentration level and the capability for release under an appropriate extraction procedure;

- 2). Adaptability to an on-site, real-time metal ion monitoring instrument, based on X-ray fluorescence emission from captured metals which would provide simultaneous

multielement analysis.

To undertake development of such a new medium, the inherent behaviour of filtration and adsorption must be assessed and their best features employed in the desired materials.

A.2 Large Volume Filtration Principles

Traditional filtration is a mechanical system for the removal of particulate matter from liquid media. The simplest process is based on the concept of physical trapping of rigid particles from small volumes of the liquid by a two dimensional porous medium. For filtration from larger volumes, depth filters are used which are composed of random mats of metallic, polymeric, or inorganic materials. These filters rely on both the porosity and tortuosity of the filtration material to trap particles. Alternatively, sieve filters, used primarily in large volume systems, trap particles larger than their void size on the top surface of the medium. Smaller particles are retained within the voids of the filtration medium. These filters generally retain large quantities of particles within the matrices. However filters of this type

are not suitable for removing particulates from large volumes of some fluids such as natural water, in which there is a wide distribution of particle sizes. For these cases, high fluid flow has traditionally been achieved, as in drinking water treatment processes, by using the third type of adapted filters, granular filter media, such as sand, activated carbon and many other substances. These granular media can tolerate broad ranges of particle size, and large volume flows. Therefore, for achieving the high throughput needed in a preconcentration analysis system designed for fresh water sources, the optimum physical form appears to be that of these granular media filters.

A.2.1 General Filtration Mechanisms

A.2.1-1 Physical Filtration

In a granular filter bed there are three physical transport mechanisms involved in capturing transported materials: interception, sedimentation, and Brownian diffusion(Fig.1). These mechanisms can all be important in the removal of particles from water. The largest particles are captured by the filter surface by a combination of intercep-

tion and sedimentation.

Interception (Fig 1-A) occurs when the particle moves with the streamlines of the fluid and, because of its size, the particle comes in contact with a stationary surface.

Sedimentation (Fig. 1-B) is

important when the settling

velocity of the particles is significantly greater than the interstitial velocity of the fluid. The particle moves downward across fluid streamlines and contacts a stationary surface. For large particles of low density, interception and sedimentation tend to be equally important in particle removal. As the density of the particles increases, sedimentation becomes dominant.

When the particles in the water are larger than the voids in a granular bed, removal takes place by a combination of these processes which is often known as "straining". Straining is significant in a granular bed filter when the ratio of the particle size to the grain size is greater than 0.2^(11,12). As the

voids become smaller, because of deposition of particles, the size of the particles removed by straining become smaller. The efficiency of particle removed by straining depends only on physical size and is not determined by the chemistry of the particles or the granular medium.

Capture of the smallest particles ($<1\mu\text{m}$) by the stationary surfaces of the filter medium is usually dominated by Brownian diffusion. For these small particles, removal depends to a significant extent on attachment by interfacial forces. In a typical granular bed, capture attributable to Brownian diffusion decreases and the removal efficiency for destabilized surfaces decreases as particle size increases above a diameter of about $1-10\mu\text{m}$. Then, interception and sedimentation dominate the capture process. As a result of this change of mechanism, a theoretical minimum efficiency of particle removal exists in the vicinity of $1-10\mu\text{m}$. This has been confirmed by experiments⁽¹³⁾.

A.2.1-2 Adsorption mechanisms

Removal of particles smaller than the voids of the medium requires transport of the particles from the fluid to the

surface of the medium(or to previously deposited particles). As the particles approach the surface, short-range surface forces can influence particles and divert them to the surface.

Recent studies show that the chemical interaction of surfaces of particles in water with the surfaces of granular filtration media can play a very important role in the filtration process^(8,9). A granular filtration system, with a surface-active particulate filtration medium or with a surface-coated chemically active medium, would combine the advantages of physical trapping with an enhanced surface adsorption capacity. This surface could be designed to have a favourable polarity effect between the medium surface and target compounds in water⁽¹⁰⁾. By this approach, the retention capacity of the medium can often be significantly increased without the loss of flow rate associated with improvements in retention achieved by reduction in pore size.

A fourth mechanism, the destabilization of the interaction surface may be the most significant process for colloidal particles because of their very low density. In this process, attachment of the particles to the surface of the medium occurs if the short-range repulsive force are minimized.

A. 2.1-3 Filter Behaviour

For filtration by any of these mechanisms, increasing the influent particle concentration has no effect on the removal efficiency. Therefore in granular filtration systems, increasing the length of the filter voids by increasing the depth of the bed or increasing the efficiency of particle attachment both increase removal. The removal efficiency decreases with increasing interstitial velocity and the diameter of the filter voids. (In a granular bed filter, the diameter of the filter void is proportional to the size of the grains in the bed.)

There is a pressure build-up, often called "head loss", during the filtration process. The rate of head loss in granular bed filters, assuming that deposition occurs at least in part within the interstitial void spaces, depends on the rate of the particle volume removal, the filtration rate, size and total volume of the interstitial spaces. The lowest rates of development of head loss and the longest filter runs are obtained when the region in which the deposition takes place is deep providing long void lengths and the medium grain size is large providing large-void diameters. Thus, the development

of head loss is minimized by use of all the void space in the bed. Low filtration rates also tend to yield low rates of head loss. For a given mass concentration of particles, increasing of particle density decreases the volume of interstitial void space consumed in the deposition process and, therefore, decreases the rate of development of head loss.

An equation used to quantitatively describe the effects of filter depth on filter performance is as follows:^(12,14)

$$\ln \frac{C}{C_0} = -\frac{3}{2} (1-f) \alpha \beta \left(\frac{L}{d} \right)$$

where f is the bed porosity, L is bed depth, d is the density of filter medium grain, c_0 and c are the influent and effluent concentrations for a packed bed, α is defined as a ratio-which compares the number of the contacts which succeed in producing adhesion to the number of collisions which occur between suspended particles and the filter media, β is a ratio-which compares the rate at which particles strike the collector to the rate at which particles flow toward the

collector. If the filtration velocity, particle size and media size, are predetermined, then, the α , which reflects the surface reactivity of the particles with the bed grains^(12,13), is the most important of the factors for establishing an optimum granular bed filtration system.

Applying this basic theory, an analytical filter is required which exhibits both strong physical trapping and adsorption capacity. According to the general filtration principles, there are two basic approaches:

- 1). Use a mix-sized granular filtration bed, which forms size-variable voids for trapping metal particulate of any size. If dissolved metal species can be converted to colloidal or hydroxide form, then they can also be physically trapped this way. The trapping can be much enhanced by the presence of fine pores in the grain surface.
- 2). The adsorption capacity of the analytical filter by coating filtration medium can be increased with specific materials so that dissolved metal species can be adsorbed on the surface of filtration medium, in a mechanism similar to coprecipitation.

A.3 Preconcentration of Trace Metal Ions by adsorption of an Intentional Macrocomponent

Although the particulate form of metal ions can be retained directly in the filter system, the dissolved metal ions in water are too small to be physically trapped in the granular filter. However, the dissolved metal ions could be chemisorbed on the filter medium surface either by changing the surface characteristics of the medium or by changing filtration conditions during trapping of the particulate metal form.

Many treatment processes ^(15,16,17) for the removal of trace quantities of inorganic species from industrial wastewaters have been reported. All these treatment processes were based on coprecipitation of microcomponents (trace metal ions) by addition of intentional macrocomponents as a kind of "flocculant". The most important macrocomponents used in the coprecipitation process are the oxides and hydroxides of iron, aluminum and magnesium.

A.3.1 Trapping Mechanisms

It is usually possible to differentiate experimentally

between two general types of coprecipitation: incorporation of the impurity into the crystal lattice of the host material and adsorption of the trace elements on the surfaces of the precipitate. For the first mechanism, the ratio of the fraction of the trace elements to the major elements precipitated is relatively independent of the precipitation conditions such as excess of precipitating agent or the presence of highly charged ions. In contrast, in precipitation of trace elements by adsorption, the ratio of the quantity of the trace to the major elements in the precipitate is influenced strongly by the precipitating conditions. This difference occurs because in the first mechanism of coprecipitation, the distribution of the trace elements in the precipitate is continuous, whereas in the second mechanism the trace elements are concentrated over the surfaces of the crystals.

The efficiency of coprecipitation by the adsorption mechanism for ionic precipitates is described by Paneth-Fajans-Hahn adsorption rule:⁽¹⁸⁾ " Those ions whose compounds with the oppositely charged constituents of the lattice are slightly soluble in the solution in question are well adsorbed

on the ionic crystal." In other words, adsorption increases as the solubility of the trace element decreases. However, the solubility is only one of the factors affecting adsorption. The other main factor is the polarizability of the ion.

If the surface sites of the adsorbent are already occupied then an exchange of the surface ions can occur with ions in the solution, e.g.,

The amount adsorbed per unit quantity of adsorbent (mol/mol)C, is given by the thermodynamic relation:

$$C = K \cdot \frac{[\text{Pb}^{2+}]}{[\text{Ba}^{2+}]}$$

where the concentrations refer only to the ions in the solution. Usually, adsorption of neutral compounds on an interface occurs by molecular adsorption. Cation-anion pairs on surfaces can act as neutrals if they occupy adjacent sites on the precipitate surface. This adsorption process is described quite well by the empirical equation of the Freundlich Adsorption isotherm:

$$C = \alpha \cdot C_0^\beta$$

where C and C_0 are the concentrations of the trace constituent in the precipitate and in the original solution, and μ and β are constant characteristic to the given system; usually, $\beta < 1$. If the precipitate has only a limited number of surface sites available for adsorption, then the Langmuir isotherm gives a better quantitative description than the Freundlich isotherm. This isotherm follows the equation:

$$C = \frac{C_\mu K C_0}{1 + K C_0}$$

where K is a constant and C_μ is the limiting value for C , which is effectively the monolayer capacity with all available sites occupied.

For coprecipitation of trace elements onto inorganic precipitates, the most common and most studied matrices are the hydrous oxides-such as $\text{Fe}(\text{OH})_3$. These are common since most metals form insoluble hydroxides at neutral pH. Various hydrate oxides have been studied, the main ones being $\text{Fe}(\text{OH})_3$ and MnO_2 ,^(19,20). However many other hydroxides are also known, such as $\text{Al}(\text{OH})_3$,^(21,22) $\text{Mg}(\text{OH})_2$,⁽²³⁾ $\text{Ti}(\text{OH})_3$,⁽²³⁾ and $\text{La}(\text{OH})_3$,⁽²⁴⁾ etc. Because most metals beyond group I of the periodic table can

be trapped effectively, coprecipitation by hydroxides or hydrous oxides is more useful for concentration of all metals of interest together rather than for separation of a particular metal. In brief, the selectivity is low. It is a very common preconcentration technique for natural dilute solutions (sea water, fresh water, treated waste solutions) in which the major constituents which are Group I ions or common anions will not coprecipitate to a significant extent, while many of the trace elements will be coprecipitated. However the matrices do vary, so that coprecipitation with MnO_2 is quite selective while with $\text{Fe}(\text{OH})_3$ it is very general.

It has been suggested that ion exchange reactions play an important role in coprecipitation reactions with hydrous oxide^(25,26). According to this mechanism, iron hydroxide acts as an ion exchanger. For simplicity, iron hydroxide is written as $(\text{FeH})_n$ exchanging with metal ion: Me . Action as an ion exchanger is then written in the form:

The distribution coefficient, D , is defined as:

$$D = C_p/C_s$$

where C is the amount of Me and the subscripts p and s denote

in the precipitate and in the solution, respectively. Applying the mass-action law leads to:

$$K = \frac{[H^+]^n \cdot D}{[FeH]}$$

indicating that the distribution coefficient depends on the pH of the solution.

By taking the logarithm and rearranging, Equation above leads to the equation:

$$\text{Log}_{10}D = n \cdot \text{pH} + \text{log}_{10}K + n \cdot \text{log}_{10}[FeH]$$

Bruninx, Upor⁽²⁷⁾ et al. found that some results follow the equation, giving $\text{log}_{10}D$ as a linear function of the pH, whereas Gadde and Laitinen⁽²³⁾ observed a nonlinear relation. In other cases Bruninx et al⁽²⁴⁾. studied the effect of pH on the coprecipitation of Zn, Cd, and Hg, using radioactive tracers, with ferric hydroxide. They found that in the pH range of 6 to 9, for all these three elements and for various concentrations and different synthetic water mixtures, there is a linear relation between $\text{log } D$ and the pH. On the other hand, it is clear in all cases that the value of n is not 2, as might be

expected from the valency of the elements, (Cd^{2+} , Zn^{2+} , etc.), This leads to the conclusion that none of these metals is bound to $\text{Fe}(\text{OH})_3$ as the bare cation Me^{2+} . The adsorbed species aside from Me^{2+} might be $\text{Me}(\text{OH})^+$, $\text{Me}(\text{OH})_2$, and similar species. From this equation it can be expected that $\log D$ will increase linearly with the logarithm of the amount of the precipitated $\text{Fe}(\text{OH})_3$. Bruninx⁽²⁷⁾ Found that the experimental results for D as a function of FeH obey this equation with reasonable agreement for the value of n as found from the experiments for Zn and Cd , but no agreement was found for Hg . Similar results were obtained by Shimomura et al.⁽²⁸⁾ Although this equation does not show a dependence of D on the amount of the coprecipitated metal (Me), usually D decreases with (Me). This phenomenon is attributed qualitatively to the limited number of iron hydroxide-free binding sites for the metal ions. Quantitatively, it was found in a number of cases that the data fit either the Freundlich or Langmuir isotherms. Freundlich isotherms were found to be more appropriate than the Langmuir form.

Bruninx found⁽²⁹⁾ that at pH 8.5 there is a linear correlation between $\log D$ and the percentage of the element present in any hydroxycomplex form (for Ca , Mn , Ge , Zn , Cu , Cd , and Pb), indicating

that the coprecipitation occurs via OH bridges. The following two possible mechanisms were suggested, where FeOOH stands for the ferric hydroxide:

1. Formation of surface hydroxycomplex

2. Hydrolysis followed by absorption

James and co-workers⁽¹⁵⁾ suggested four different models to describe the distribution of metal ions between the solution and the interface of the precipitate. These four models have different physical representations concerning the coordination, hydration, and size of the adsorbed species and the source of H^+ , but lead to similar quantitative expressions.

Model I: Ion exchange - It assumed that the coprecipitation is due to the simple "ion-exchange model" and considers the reaction of the free metal ion with surface hydroxyl group to be formation of a coordinate metal-oxygen bond with the release of H_2O and H^+ : ($\bar{S}$: Total Surface; H: Hydrogen; S: specific surface site)

where m and n are not necessarily equal numbers. The value of n may vary with the pH. The distribution coefficient of the metal between the surface and the solution is given by the equation:

$$D = \frac{\text{mol} \cdot \text{kg}^{-1} \text{surface}}{\text{mol} \cdot \text{l}^{-1} \text{solution}} = \sum_{i=0}^n \frac{K_i \overline{SH}^i}{(H^+)^i}$$

For metals which form coordination complexes with OH and other ligands, the ion exchange of all existing species should be considered. The pH dependence of the distribution coefficient is given by the equation:

$$D = \sum_{i=0}^n \frac{\alpha_i}{(H^+)^i}$$

Model II: Surface hydrolysis - This model assumes that adsorption is followed by surface hydrolysis:

Model III: Adsorption of hydrolytic complexes - The aqueous metal

ions are hydrolysed to hydroxycomplexes which are adsorbed to the surface by oxygen atom bridges.

Model IV: The adsorption is assumed to occur by the formation of low-to high-molecular-weight polymeric hydrolysis products which are adsorbed on the interface by large van der Waals' attractive forces. The hydrolysis of the metal ion in the course of sorption was explained in various ways (1) interaction with the surface hydroxyl groups, (2) simultaneous passage to the sorbent surfaces of aquacomplexes with hydroxyl ions, and (3) a substantial increase in the concentration of the microcomplexes in the solid phase of the sorbent in comparison with the solution. From the models above, James et al, suggested that positively charged hydroxycomplexes $Me(OH)^{2+}$ and $Me(OH)^{1+}$ do not interact with the precipitate.

Plotnikov and Safonov studied in a series of articles various factors connected to the basic information concerning coprecipitation with $Fe(OH)_3$.^(30,31,32) They also concluded that the main coprecipitable form of the hydrolysable elements studied (Sn, Fe, In, Cr, Be,

Cd) is the neutral hydroxycomplex $Me(OH)_n^0$. The pH values of the beginning of the coprecipitation (pH_c) was found to be dependent on the threshold pH for precipitation of the collector macrocomponent (pH_b), the pH of disappearance of positively charged hydroxycomplexes of the macrocomponent (pH_i), and the pH of the beginning of formation of neutral hydroxycomplexes of the microcomponent (pH_n), in the following way:

1. If $pH_n > pH_i > pH_b$, then $pH_c = pH_i$
2. If $pH_i > pH_n > pH_b$, then $pH_c = pH_n$
3. If $pH_i > pH_b > pH_n$, then $pH_c = pH_b$

In other words, $pH > pH_b$ is essential since there will not be coprecipitation if there is no precipitation of the macrocomponent. Also, it is required that either the positively charged hydroxycomplexes of the macrocomponent will disappear by chemical reconstruction to the neutral hydroxycomplexes of the microcomponent in order to lead to the coprecipitation. The pH values for the maximum coprecipitation of the hydrolysable element are those at which the corresponding unchanged complex is formed. The desorption of the microcomponent at high pH is due to the formation of anionic hydroxycomplexes.

In order to disclose the essence of the acid-base interaction

of the metal ions, the interaction of the ions was studied by a spectrometric method.⁽³³⁾ It was concluded that the interaction is based on a reaction of neutralization of the acid and base properties of the interacting metal ions by the formation of the bridge bonds between them through common hydroxyl groups. The less acidic metals donate hydroxyl groups which are accepted by the more acidic metal ions under the given conditions. Consequently, there is a weakening of the donor metal ions and an increase in the hydrolysis of the acceptor metal ions. When the pH is raised sufficiently for unchanged hydrolysed forms to appear, the formation of bridge bonds between the interacting metals increases. This bond is due to the participation of hydroxyl groups of the inner sphere of the hydroxylcomplexes of both metals. This study indicated that the coprecipitation of mainly unchanged hydroxycomplexes is due to the ability of these particular hydrolysed form of metal ions to form bridge bonds with the participation of the hydroxyl group of the both the micro- and macrocomponents.

In summary, from the previous research on both the principles of filtration and on adsorption theory, it seems possible to build an analytical filter for preconcentration of both particulate and dissolved metal ions from raw turbid water. By forming a

surface favourable to adsorption on the granular solid matrices as combination of chemical and physical trapping of neutral hydroxy complexes will allow determination of heavy metal ions at or under ppb level in water.

B. EXPERIMENTS

B.1 Experiment Design

B.1.1 Search for a High Volume Capacity Analytical Filter Medium

Analytical filtration has traditionally been done using binderless membrane filters made of glass or organic polymers. However, retention of small particulates or colloids quickly results in plugging so that analytical filtration of large volumes becomes impractical. For filtering high volumes, cartridge or tubular type filters are available commercially. However, for turbidities encountered in fresh water these filters also quickly plug up, again limiting the sample volume. To recover and analyze the solids, these filters need large soxhlet extraction equipment, large volumes of solvent and lengthy extraction procedures. Both the limits on filtered volumes and on subsequent analysis volumes make these conventional procedures costly and time consuming.

In this study, research has been directed towards the development of an alternative filter system which would allow

the efficient filtration and then convenient analysis of large volume of turbid water. Following the discussion of alternatives, attention was been focused on the development of granular media filters. Traditionally, these filters have been used only for water treatment processes^(34,35,36) and no previous attempt to use them for any analytical purpose has been reported. However, since these filters can accommodate large volumes, and can be essentially free of contaminants, it was important in this investigation to see if some granular media filters could be used as analytical filters for turbid fresh water. Accordingly, a number of granular materials were chosen for study based on their retention capacity of particulate matter from water at various turbidities.

Among the prospective granular filter media identified in the first survey, Celite was identified as particularly promising physically and chemically. It has traditionally been used as a highly effective filter aid. But there is no previous report of its use as an analytical filter medium. Celite is the trade name for a form of diatomaceous earth sold by Johns-Manville Corporation. Diatomaceous earth is comprised of extremely tiny fossil-like skeletons of microscopic

material (Photo. 1). Each skeleton is an extremely porous framework of nearly pure silica. Diatomaceous earth is known to be well suited for filtering out very minute particles from water, and has a very high particle retention capacity. The physical stability, the high surface properties for the retention of particulates, the very low extractibility and chemical inertness of Celite under various conditions would make it an excellent analytical filtration device. Thus, of the available media it presented the best option for detailed study in a potential analytical filtration system.

B.1.2 Bench Scale Study of Heavy Metal Retention in the Filtration System

In natural water system, the heavy metals, like the organic pollutants, are distributed between the particulate and the aqueous phases. Preconcentration of dissolved heavy metals using the APS II sampler with conventional trapping media poses a particularly difficult problem. Preconcentration of the trace level dissolved organic pollutants in water using XAD-2 resins can be accomplished readily, but retention of the dissolved heavy metals has proven unsatisfactory^(5,6). The use of

organic chelating agents adsorbed on XAD column has been suggested⁽⁶⁾ for the preconcentration of dissolved heavy metals from a large volume of water. However, even this modification has severe limitations, since the complexing abilities of organic ligands vary widely for different metals. Using a single immobilized ligands, a quantitative retention of all the heavy metals is not feasible. Also, for ligands immobilized by hydrophobic bonding to XAD, the use of acids to extract the adsorbed metals from the resin column liberates large quantities of the ligands. This contamination of the eluent usually complicates the subsequent analytical process. To overcome these problems, alternative methods of trapping heavy metals have been attempted.

Coagulation of suspended materials using salts of aluminium, iron or manganese. has traditionally been used for the removal of heavy metals as well as organic pollutants from drinking water⁽³⁴⁾. Alternatively, chelation using organic ligands and subsequent solvent extraction and co-precipitation using hydrated oxides of aluminium, iron, magnesium, manganese, titanium have been used for the coprecipitation of trace level heavy metals from grab water samples as described

in the Introduction. These methods suggest that coprecipitation techniques in conjunction with granular filtration media, could be used to avoid using a separate resin column for the preconcentration of the dissolved heavy metals. A single chamber filter with granular filter media, coated with coprecipitation substances, should retain heavy metals in both particulate and dissolved forms, and still permit continuous flow of high volumes of test water.

A bench scale study was designed to study the feasibility of using the Celite filter medium to trap the heavy metals in water. Using the same apparatus, similar experiments were designed to study the effect of precoating the Celite granular medium with some metal hydroxides on the retention of heavy metals. Results from these preliminary experiments were then intended to guide the adaptation to the APS II system.

B.1.3 APS-II Preconcentration System

Some technical problems were anticipated in adapting the these techniques to the APS II system. The agents used to precipitate the soluble metal ions could not be added to the bulk of the test sample at one time, because the resulting

insoluble material would settle before. Instead, in one option, the sampler was adapted to allow addition of these agents to the sample stream via a side port by dynamic spiking. The other alternative was to pre-treat the Celite granular medium with the metal hydroxide settling agents. This allowed a test of the ability of immobilized colloids to trap pollutant metal particulates at the time of filtration. Since these two approach are not mutually exclusive, side port dynamic spiking of precipitating solution would let dissolved heavy metal ions form hydroxide precipitate which could then trapped by the immobilized colloids. This combined approach would make an even more reliable trapping of heavy metal pollutants. This adaptation seemed to be the most attractive from a practical point of view. The optimum conditions, obtained from the bench scale studies, were used for APS-II system study, at a flow rate of inlet at 100mL/min.

B.2 Materials

B.2.1 Filter Media.

All test materials used as granular media namely Celite,

Activated Carbon, Granular Activated Carbon(GAC), Silica Gel, Cellulose powder, Sephadex gel, Sand were obtained from commercial sources and used without further treatment except Celite. Celite is a calcined diatomaceous earth produced by John Mansville Corporation.

B.2.2 Labware

- Nalgene polyethylene bottles, 1 litre, 50 mL.
- Polyethylene volumetric flask, 50 mL .
- Polyethylene pipettes, 10-50 μ L, 50-200 μ L, 200-1000 μ L, 2 mL, 10 mL.
- Cambridge depth filter paper, pore size 1 μ m.
- Membrane filter, pore size 0.45 μ m.

B.2.3 Chemical Reagents

- Nitric acid, J.T. Baker Inc., Heavy Metals less than 0.05ppm.
- Metal Standard Solution, BDH Inc, 1000ppm each. (Pb, As, Cu, Cd Cr and Hg).
- $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, BDH Inc. Heavy Metal Residue 0.5 - 2.0 ppm.
- Alum, J.T. Baker Inc. Heavy Metal Residue less than 3 ppm.

(The higher purity of aluminum salt should be used if heavy metal concentration in water sample less than 100 ppt).

- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, BDH Inc, Heavy Metal Residue 5 ppm.
- NaOH, BDH Inc. Heavy Metal Residue less than 0.5 ppm.
- Water, Deionized Distilled, Barnstead Nanopure Water System.

B.3 **Equipment**

- Automatic Preconcentration Sampler (APS-II), Inorganic System. Inlet water passing through the system by suction.
- Atomic Absorption Spectrometer (Varian 20) with Furnace (GA-96) and Automatic Sampler.
- pH Meter , ORION-520A, ORION Research Inc. Boston, USA.
- HACH Ratio Turbidimeter, HACH Company, Loveland, Colorado.
- Filtration system linked in series of pump, pressure gauger and filter holder. Inlet water passing through the system by pumping.

B.4 **Cleaning Procedure for Labware**

All labware used were cleaned with a sequence of steps:

- 1). soap solution; 2). tap water; 3). 15% nitric acid; 4).

distilled water, then dried in oven at 110°C.

The APS-II Cleaning Procedure followed the method described in "the Final Report of APS-II", Department of Chemistry, Carleton University.⁽⁵⁾

B.5 Preparation of Heavy Metal Standards

Six metals from the list of target metals were chosen for the studies. Metal standards from BDH Inc. of copper, chromium, mercury, lead, arsenic, and cadmium (1000 ppm each) were diluted to 10 ppm each by adding 1 mL of each standard to a 100 mL volumetric flask. The volumetric flask was then stoppered and sealed with parafilm. Periodic testing of the sample showed that the metal concentrations were not measurably altered by long storage periods.

B.6 Raw Water Standard

The constituents chosen for the raw water standard included illite and vermiculite clay minerals, quartz, humic and fulvic acids in proportions to mimic natural waters⁽⁶⁾. The solid materials were crushed and milled to approximately 300 mesh grain size, and the fraction greater than 45 μm was

eliminated by dry sieving. The raw water standard was established as a 500 NTU turbidity stock suspension containing 130mg humic acid and 130 mg fulvic acid, 1670 mg illite, 670 mg vermiculite, and 670 mg quartz in 1 litre of water. This stock solution was diluted appropriately to obtain various turbidities used in testing the filters. The sample was agitated with a stirrer during the run to maintain the uniformity of the suspension. The turbidity of the influent as well as the effluent was measured by using a HACH Ratio Turbidimeter.

B.7 Filtration Test of Various Media

All the experiments were carried out using a 4.7cm diameter polycarbonate Gelman filter holder with a 1 μ m Cambridge GF filter paper at the base to hold varying quantities of granular media. In some studies, an additional membrane filter (0.45 μ m pore size) was used below the Cambridge filter. Water samples of various turbidities were either pumped through the filter by a hydraulic pump or were drawn through it using the APS II sampler. The APS II system was modified by eliminating the reservoir and by replacing the

old filter unit with the one described above. The efficiencies of the filter systems were evaluated from (1) the volume of water passed through the filter, (2) back pressure (headloss) developed at the end of the run and (3) the turbidity of the effluent water. The media tested were Celite, Activated Carbon, Granular Activated Carbon (GAC), Silica Gel, Cellulose Powder, Sephadex, and Florisil.

B.8 **Filtration Test of Celite with Different Amount and Particle Size**

After these initial efficiency tests, Celite was chosen as the filtration medium for further investigation. Tests to compare its filtration efficiency with varying amounts and particle sizes were carried out as in method B.7 except that the 4.7cm Gelman filter holder was modified to form a 4.7x20.0cm³ cylindrical filtering unit for the experiments.

A study of various volumes of water passed with various NTU influents was also carried out using a constant amount of Celite in the filter.

B.9 **Tests of Acid Pre-washed Celite in terms of Heavy**

Metal Residue and Filtration Efficiency

20 grams of Celite were washed with a 15% nitric acid solution three times (100ml each , filtered, then washed with 300ml ultrapure water and dried in oven at 110 C for over night. Then 2.50 gram of acid pre-washed celite was extracted two times with 50ml of a 5% nitric acid solution. Heavy metal residues in the 100ml combined extracts were determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

A control test of the filtration efficiency of acid pre-washed Celite and non-washed Celite was designed using same amounts of Celite and 5 NTU turbidity water.

B.10 Bench Scale Study of heavy metal Retention Capacity of Celite and Celite with Additives under Various Conditions

B.10.1 Filter and Sample Preparation

Bench scale investigations were carried out to determine the feasibility of using a granular Celite-based filter for the preconcentration of heavy metals in water. Both reagent water from Barnstead system and Rideau River water obtained

from a test site giving clear surface samples were used for spike recovery studies. A modified Gelman filter holder ($4.7 \times 20.0 \text{ cm}^3$) made of polycarbonate and containing 5g of Celite supported on a 4.7cm GF Cambridge filter was used for most of the studies involving the heavy metals. The granular Celite was precleaned by thorough washing with 15% nitric acid. A spiked sample of 200mL was treated with nitric acid or sodium hydroxide to bring it to a desired pH and was passed through the Celite-based filter. Then 1mL of concentrated nitric acid was added to 100mL of the effluent and analysis for the heavy metals was carried out. A blank was run with corresponding conditions but without spiking.

B.10.2 Heavy Metal Retention of treated and untreated Celite

The precleaned Celite was impregnated with hydroxides of aluminium, iron, magnesium in the following way. To a 500mL beaker with 100ml ultrapure water, 0.2mmol of alum, FeCl_3 , or MgCl_2 , was added along with 5 grams of the precleaned celite. The metal hydroxide was then precipitated by slowly adding

0.2M sodium hydroxide solution with slow stirring. The precipitate was adsorbed on the Celite which was separated and washed two times by decantation. The spiked water samples were adjusted to various pH values in the range from 8 to 11 and passed through the metal hydroxide coated Celite filter. Then 5 grams of precleaned but untreated Celite was tested for heavy metal retention by the same method as used for treated Celite. The trapping capacity of heavy metals in each case was evaluated by determining the target metal ion concentration in the effluent by GFAAS.

B.10.3 Various Coating Quantities of Aluminum Hydroxide on Celite for Heavy Metal Retention

Heavy metal retention capacity of the Celite impregnated with different levels of aluminum hydroxide was studied at the optimum conditions of pH determined in the experiments described in B.10.2.

B.10.4 Heavy Metal Recovery

The efficiency of recovery of heavy metals from the filter was studied by using 2% and 5% nitric acid. After

passing a spiked water sample through the filter, the filter media (the coated Celite and Cambridge filter paper) were carefully transferred to a 500ml beaker. Then 100mL of the extraction solution was added to the beaker after it had been used to rinse the filter holder thoroughly. The beaker was then placed in an ultrasonic water bath and ultrasonicated for 15 minutes, then filtered with Whatman quantitative paper. For spiked ultrapure water, sample extraction was repeated once. For spiked river water, extraction was carried out three times. The conditions of the filter and sample were set according to optimum conditions determined in the experiments described in B.10.3.

B.10.5 Analytical Controls

The blank was obtained by adjusting the pH of 200mL ultrapure water which was then passed through the filter under conditions identical to the specific study.

For all of bench scale studies, the heavy metal retention capacity was determined by measuring the metal ion concentration in the effluent except for the experiment described in B.10.4., in which it was determined from the

extracts. No suction or pumping was performed during the bench scale studies. Duplicates were done for the most of experiments.

**B.11 Recovery Study of the Heavy Metals Using the APS-II
 Inorganic Sampler**

The optimum conditions for the trapping of the heavy metals, obtained from the bench scale study described in B.10, were used in the studies with the APS II system. All spike recovery studies were carried out using 10 L of reagent or Rideau river water and by using the filter systems described in B.10.3 with a flow rate of 100 ml/min. A blank run was carried out before each experiment. The spike solution and 0.2M sodium hydroxide solution (for the adjustment of pH) were introduced into the sample stream via side ports at an average rate of 5ml per litre of the sample. By monitoring pH of the effluent from the filter, the rate of addition of base was adjusted to keep the pH to the desired value. After each run the filter was extracted with 5% nitric acid solution and extract was analyzed for the heavy metals by using GFAAS.

B.12 **Microstructure of the Celite**

The microstructure of the Celite was investigated by examination with an electromicroscope. The samples observed were Celite, Celite coated with aluminum hydroxide, and Celite coated with aluminum hydroxide through which a heavy metal solution had been passed.

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C. RESULTS

C.1 Filtration Tests

C.1.1 Performance of the Granular Media

Filters

The performance characteristics of various filter media along with those of some conventional filter papers are shown in Table 1. The data for the first four filter media were obtained using the pumping mode of filtration. The rest of the data were obtained through the APS suction mode. These initial results showed that Celite has a outstanding performance in filtration efficiency. Therefore, the efficiency of the Celite filter in terms of total volume of fluid filtered, the depth of the filter media used, input and output turbidity, the back-pressure developed, and the effect of the size of the Celite grains etc. were studied.

C.1.2 Celite grain Size

The grain size of granular filter media has a strong effect on the efficiency of filtration as was reported by other workers⁽¹⁶⁻¹⁸⁾. The results of the present study, which was

carried out by using the suction mode of filtration, are shown in Table 2 and Fig.2. As a predicated by models, mixed grain size of Celite gives higher throughput than either a uniformly smaller or uniformly larger grain size.

C.1.3 Filtration Mode of Pumping & Suction

A comparison of the efficiency of the two modes of filtration in terms of total volume filtered, output turbidity and headloss development is shown in Table 3. It is seen clearly that the pumping mode of filtration is much more efficient than the filtration by suction through the filter. In suction mode, when the filter was blocked (around 14 psi) many bubbles appeared and the flow could not be maintained at 100ml/min. In the pumping mode, the flow rate can be maintained by applying pressure to the filter. However, the maximum practical pressure was less than 25 due to the limitations of the tubes and unions.

C.1.4 Volume of Water Filtered vs Amount of Celite in the Filter

The figure 3. shows the relation of the volume filtered with fixed turbid water to the amount of Celite in the filter. The highest filtered volume was obtained with 5-10 grams of Celite in the filter. Lower or higher amounts of Celite result in lower water volumes.

C.1.5 Output NTU vs Volume of Water at Various Amount of Celite

For a fixed input turbidity, the output turbidity drops immediately below 1 NTU and then slowly decreases to lower values as the volume of water filtered increases. As expected the quality of the filtered water (in terms of low and consistent turbidity) increases as the depth of the filter column increases. This is demonstrated in Fig. 4.

C.1.6 Backpressure vs Litres of Water Run

The relationship of back-pressure to the depth of the Celite as filtration progresses is showed in Figure 5. With an increase in the depth of the filter column, the back-pressure develops at a faster rate, and the volume of water filtered is

reduced.

C.1.7 Acid-Washed & Non-washed Celite

The comparison of filtration efficiency of acid prewashed and non-prewashed celite is showed on Table 5. There is no significant difference in behaviour between the two materials. The Celite is prewashed with acid as a precaution to remove any possible heavy metal residue before use in trapping heavy metals from sampled water. The result indicates that acid washing does not destroy the fossil-like skeletons or the tiny pores on the surface of the Celite.

C.1.8 Celite Filtration with & without Supporting Membrane Filter

The turbidity of water coming out of the filter can be further reduced by placing a $0.45\mu\text{m}$ membrane filter below the Cambridge filter. However, back-pressure development rapidly builds up and the output filtered volume is reduced. This is shown in Table 6.

C.1.9 Effect of Turbidity of Sampled Water

Under the same filtration conditions used to test Celite performance, a plot of total volumes of the output vs various input turbidities is shown in Fig. 6. The higher the input turbidity, the lower the total volume of water that can be passed.

C.2 Bench Scale Study of Heavy Metal Retention **in Celite Based Filtration System**

C.2.1 Heavy Metal Residue in Acid-washed Celite

The heavy metal residue in acid prewashed celite was extracted with 2% & 5% nitric acid and determined by using GFAAS. Table 7 gives the results, which are the average of two duplicates. It is seen that in both extract fractions, mercury is not detected and arsenic is present at the level of 0.2ppb in the 5% fraction. Copper and chromium are present in very low amounts, and the one present in the largest amount, lead, is only around one ppb. To avoid these background levels in subsequent tests, acid-washed Celite was used for trapping heavy metals in the following experiments.

C.2.2 Retention of Heavy Metals on Treated Celite as a Function of pH

Heavy metal retention at various pH values are compared between untreated Celite and the Celite treated with the hydroxides of magnesium, iron and aluminium. The results, shown in Table 8 and Fig. 7, indicate that the all three hydroxides show comparable trapping effectiveness, but that aluminium hydroxide treatment gives the best overall performance. In contrast, the untreated Celite shows significantly lower heavy metal retention capacity.

C.2.3 Relation between Aluminum Hydroxide Loading on Coated Celite and Heavy Metal Retention Capacity

Table 9 and Fig. 8 shows the effect of the three levels of aluminum hydroxide coating Celite on the percentage of heavy metals trapped at constant pH. Loadings of 0.2 and 0.3 mmol of aluminum hydroxide per gram of Celite display the same trapping capacity, although a slight difference is seen with some metals. The 0.1 mmol/g coating level appears to give an

overall lower of trapping efficiency.

**C.2.4 Influence of pH on the Retention of Heavy
Metals**

The trapping efficiencies of the hydroxide coated Celite for the heavy metal spiked ultrapure water and Rideau river water samples at various pH levels are shown in Table 10 and Table 11 respectively. The relation between percentage recovery of various metals and pH are shown in graphical forms in Fig. 9 and Fig. 10 for ultrapure water and Rideau river water respectively. The retention of lead, cadmium and mercury by the filter medium increases steadily with the increase in pH. These metals are retained quantitatively at pH 12 from both ultrapure water and river water. For chromium, copper and arsenic, the retention efficiency goes through a maximum and decreases at higher pH, probably due to the formation of oxygenated anions. In general, the retention efficiency of the Celite medium for the metals is better for river water than for ultrapure water. This effect is very pronounced for chromium (Table 10 and Table 11). These results confirm the

data shown in Table 8 which indicate that the preconcentration of a particular metal depends on an optimum pH value for that metal.

C.2.5 Extraction Efficiency of Heavy Metals from the Filter

The extents of extraction of heavy metals extracted from coated Celite are shown in Table 12 and Table 13 for spiked ultrapure water and spiked river water respectively. From both sources, the first 100mL of extraction solution accounts for 50% or greater recovery of all of the six metals, except chromium in spiked ultrapure water. From the spiked river water samples, a third 100ml extraction solution was used, which increased the recovery rate for all of the metals. For lead, cadmium, and mercury the total recovery rate of each is 90% or higher from both spiked ultrapure water and spiked river water. For copper, the recovery is acceptable in both cases. The recovery rates of chromium and arsenic were relatively higher in spiked river water, with an especially remarkable increase observed for chromium. This correlates

with the trend seen in Table 10 and Table 11. Chromium appears to be captured by biotic matrix in natural water, then trapped by filter.

C.3 Validation Studies of Inorganic APS-II Sample in Preconcentration of Heavy Metals

Spike recovery studies using the modified APS II system were carried out under the optimum conditions established in bench scale experiments. The results for ultrapure water and Rideau river water are shown in Table 14 and Table 15 respectively. These are compared with the results of the corresponding bench scale study. As previously observed in bench scale studies, the recovery rate is better from river water than from ultrapure water. Although a direct comparison of the results from the bench scale study with that of the APS II system is not possible because of the increase in volumes and flow rate, the two sets of results shows parallel features. No obvious reason for the poor recovery rate of Hg with the APS II system is apparent.

D DISCUSSION

D.1 Media of Preconcentration

The continual reduction in permissible exposures to toxic chemicals has emphasized the need for simple and convenient analysis of trace levels of pollutants in water. In general, concentrations of pollutants can be determined directly down to detection limits of one ppb. In the cases of all metal studied here, detection limits are possible at ppt levels by the most sensitive types of ICP-MS systems.

However, these precise and accurate systems are too delicate and expensive to use in routine monitoring of industrial process water or in emergency analyses at remote sites. The alternative strategy for obtaining trace analysis in these conditions is preconcentration of pollutants to levels which may be detected on portable and inexpensive detectors. With such equipment, sampling and detection can be performed on-site in a minimum time. Thus, instead of the delay and expense encountered with conventional grab sampling followed later by analysis in a remote laboratory, on-site determination allows a timely response to control any unacceptable contamination.

Across a wide range of simple portable detectors, the

detection limits usually imply that 1 ng of the pollutant is needed for an acceptable determination. The preconcentration apparatus must, therefore, be capable of acquiring this quantity from the water matrix in an acceptable time period and guarantee it to be free from contamination. Often this implies that large volumes of water must be processed to acquire the necessary quantity of contaminant. Typically, 10 to 100 L of water may be required to accumulate 1 ng of substance.

Two approaches are possible. One is the settling of contaminants from the still water matrix. If contaminants are colloidal however settling may not occur. In these conditions settling agents may be used to coprecipitate the contaminants. Typically, magnesium, aluminum or iron hydroxides have been used. The separation of hydrolysed toxic metal hydroxides by these methods is very effective. This suggests that the capture of these hydroxides by the hydrolysed magnesium or aluminium may involve chemical reactions as well as physical trapping. The major shortcoming, from an analytical point of view, is that this is a batch process which is incomparable with on-line monitoring.

The second approach is trapping of contaminants from a moving water stream into an extraction medium. This has the advantage that it is adaptable to continuous monitoring.

However it also requires efficient interaction of a solid phase with the liquid stream. This requirement can result in two types of limitations on the efficiency of preconcentration. If the solid phase is a two dimensional porous membrane, the particulates normally attempt to follow the liquid stream through the pores, resulting in eventual physical blockage of the membrane. If the blockage occurs before sufficient accumulation, the only remedy is a larger surface area. For large volumes this rapidly becomes too inconvenient even when convoluted or depth filters are used. If the solid phase is, instead, a three dimensional beaded material, physical trapping is poor but chemical immobilization can be very efficient. However, conventional plastic beaded materials often cause contamination of adsorbed material from the subsequent coextraction of plasticizer chemicals and heavy metal with the trace levels of adsorbed contaminants.

In the current study, a preconcentration process has been designed which attempts to use the advantages of both the settling and straining processes while avoiding these limitations as far as possible. The most advantageous aspect of the settling method is the probable chemical interaction between the medium and the contaminant. In the straining process, the valuable aspects are the continuous flow and the

potential combination of physical and chemical immobilization. Taken together, these properties suggest that an efficient preconcentration system should be based on straining from a moving stream. However, the straining should be performed in a three dimensional dispersed medium with a chemically reactive surface to maximize immobilization while avoiding blockage of flow. The medium should avoid organic supports to avoid contamination but carry a colloidal surface which is best adapted to capturing a colloidal contaminant.

When all these factors were combined, the most effective system was identified as a flow column charged with granular inorganic media. Of these media, diatomaceous earth, in the commercial form Celite gave the best performance in immobilizing contaminants from fresh water sources (Table 1).

D.2 Diatomaceous Earth as a Physical Filter

The standardized fresh water prepared for these studies was initially prepared as a suspension of finely divided but chemically inert minerals. This suspension provided a range of turbid water samples which could be used to test the efficiency of physical trapping alone, through the straining or sedimentation processes.

From these tests, (Table 2 and Fig.2), a mixed grain size bed of Celite gives a higher throughput of test standard

waters than beds of small or large uniform grain sizes. From the basic properties discussed earlier, this is expected since a mixed grain size builds a bed with variable void diameters which can trap a wide range of particles from water through the straining mechanism. Beds of grains of equal size tend to pack more evenly and more densely. Thus, particles are more likely removed from the test water by the sedimentation mechanism, to form a layer of settled precipitate on the surface of the filter bed. In comparison to the continued availability of channels through variable voids, the settled layer in beds of uniform voids behaves more like a film which can be blocked like a filter membrane. Thus, the flow for uniform beds is reduced compared to non uniform beds.

The effect of varying the depth of the bed is seen in Fig.3. The optimum throughput is achieved at intermediate depth. At shallow depths, the medium rapidly reaches its straining capacity and that then process changes to sedimentation. At the deep bed limit, flow rates become slow for distilled water and the addition of trapped solids raises the back pressure above practical limits.

The same phenomena can be observed in the variation of the quality of effluent water. As shown in Table 4, the quality increases as the depth of the bed increases. Likewise, at any depth, increased input turbidity leads to reduced

throughput because of sedimentation blockage. Addition of a support membrane at the bottom of the bed also increase output quality, Table 6. However it rapidly reduces the rate of throughput because of membrane blockage.

D.3 Diatomaceous Earth as a Chemical Trap

Diatomaceous earth is the exoskeletal remains of microscopic plants. These siliceous hollow shells are vigorously cleaned and made available commercially as Celite. In this form the material shows very low levels of extractable contaminants. The extractability of heavy metals in the acid washed particulates is shown in Table 7.

In addition to the physical capacity to trap suspended particles however, the acid washed Celite displays a capacity to chemically immobilize hydrophillic colloidal material from test water. Celite is known to carry "activated" hydroxyl groups on its surface, capable of forming hydroxy bridge bonds with these hydrophillic colloids.⁽³⁷⁾ In this study, Celite shows a significant ability to trap heavy metals as shown in Table 8 and Figure 7. due to these surface functional groups.

However, the cleaning process, involving acid wash and heat, tends to anneal these surface sites to destroy the most of their active sites. Thus, although acid washed Celite still displays a detectable chemical bonding ability, this ability

could be improved with a freshly deposited metal hydroxide surface. In this situation, the role of the hydroxyl groups on the original Celite surface become the retention of the surface coating of amorphous metal hydroxide coprecipitation material.

As discussed in the introduction, two features of this fresh surface can be exploited in maximizing the trapping capacity. One is the physical effect of coprecipitation by a straining mechanism. Here, the new surface acts like the settling agent in drinking water clarification by trapping the contaminants within the open amorphous lattice of the immobilized colloid. The other is the chemical effect of bridge-bonding. By deliberately selecting metal hydroxide colloids as the fresh surface, new, more active hydroxyl groups become available for condensation reactions with hydroxy colloid contaminants from the water phase.

The hydroxyl colloids which are most commonly used in settling are the hydroxide dispersions of aluminum^(21,22,23), magnesium⁽²⁴⁾ and iron^(25,26). All of these are efficient in coprecipitation of colloidal suspensions from fresh water. This process of coprecipitation appears to occur mainly between the neutral hydroxy complexes of the settling agent and the suspended materials. Being neutral, both materials have the common property of hydrophobicity which allows them

to associate without charge repulsion and to be mutually adsorbed on the interface by large van der Waals attractive forces.^(30,31,32)

Beyond the coprecipitation mechanism, exhibited by all the settling agents, the aluminum dispersion appears to be the most efficient trapping medium as shown in Figure 7 and table 8. This correlates with the higher acidity of aluminum hydroxide, compared to that of either magnesium or iron hydroxides. This correlation to acidity suggests that, after physical and van der Waals adsorption between the neutral hydroxy complexes of the settling agent and the suspended materials, the increase in trapping efficiency is due to a chemical interaction between the aluminum hydroxide surface and the suspended hydroxy colloid. This chemical interaction is most probably a condensation reaction, in which hydroxyl bridge bonds are formed at the surface, with the elimination of a hydronium ion.⁽³³⁾ This "chemisorption" of the suspended colloid eventually builds the trapped hydroxyl material irreversibly into the structure of the aluminum hydroxide surface. In this reaction, the integrity of the original suspended particle is entirely lost so that this original colloidal particle cannot be released back to the water phase during further water sampling.

D.4 Trapping of Trace Heavy Metals

The hydroxides of the heavy metal pollutants in fresh water are essentially incorporated into the suspended aluminosilicate colloids within appropriate pH ranges. In general, transition metal and p block metal ions hydrolyse to hydroxyl bridged colloids at or above pH 5. At higher pH levels, these heavy metal colloidal particles can coagulate with those of the more abundant aluminosilicate colloids present in most fresh waters. At very high pH levels, some amphoteric transition metal ions may redissolve as mononuclear oxyanions, so that intermediate pH ranges are expected to provide optimum chemical coprecipitation conditions.

Since the aluminosilicate carrier in fresh water is normally more abundant than competing organic ligands, the capture of the aluminosilicate carrier of river water in these intermediate pH ranges should therefore provide the highest trapping efficiencies into the immobilized aluminum hydroxide surface on Celite. This is illustrated in the data of Figure 9 and Figure 10. The p block metals are trapped with increasing efficiency up to pH 12. In contrast, the transition elements are most efficiently trapped at intermediate pH levels and show the predicted amphoteric behaviour at pH 12. Similar behaviour is seen for the p block metalloid arsenic which is probably trapped as a hydroarsenate anion.

In general the pH range from 10 to 11 can be identified as the optimum operating condition for trapping a wide range

of heavy metals. The importance of the coprecipitation mechanism becomes clear in comparing the efficiency of trapping from spiked distilled water and spiked river water. Except for the copper, the recoveries from river water are same or significantly higher, indicating that the naturally occurring suspended aluminosilicate-organic colloids play the role of capturing the heavy metal colloids first by absorption or chemisorption mechanism.

In the river water, deliberately spiked metal ions used for calibration also form hydroxides which can adhere onto aluminosilicate-organic colloids, along with those original heavy metal colloids. These colloids then build into the immobilized aluminum hydroxide surface supported by the Celite through the combined chemical coprecipitation mechanism. In this process, a condensation reaction would occur, forming a hydroxobridge and eliminating H_2O^+ , which can be neutralized by controlled addition of base to the sample stream. This process makes the chemical coprecipitation or chemisorption mechanism essentially irreversible. This loss of independent structure of colloid particles into the chemisorbing surface means that any subsequent colloid particles then encounter a new active hydroxy colloid surface on the Celite. Thus, continuous filtration will occur as chemisorbed colloids continuously form a new surface for coprecipitation. Eventually they will reach the maximum occupation of all the voids originally available between the aluminum hydroxide

coated Celite grains. The absence of this mechanism in the spiked distilled water reduces the recoveries.

The continuously spiked alkali solution in the sample stream could also stabilize the bonding between some heavy metals and the natural organic ligands present in sampled river water. This could lead to a competitive equilibrium system against the trapping surface which could slightly reduce the retention of some heavy metal, such as copper.

D.5 Scale-up to APS-II Operation

The preparation and use of these trapping media of aluminum hydroxide coated Celite in the APS-II system presented no major difficulties. The scale-up to high flow rates or throughput of water showed equivalent recoveries to the bench scale experiments. Again, recoveries from river water were the same or significantly higher than those from spiked distilled water, especially for chromium and arsenic (Table 14 and Table 15).

The recovery of mercury in the APS-II system did not reproduce the recovery in bench experiments. The reasons could be in three aspects. First, plastic in APS could leach free radicals which cause reduce Hg^{2+} to Hg^0 . The electrostatic charge on plastic surface due to flow of water could reduce Hg^{2+} to Hg^0 . The third, mercury does not form $\text{Hg}(\text{OH})_2$, instead it forms HgO which will not be trapped as same way as other

metals since it is not colloid, instead it will be carried through the filter. However mercury is the only element tested which is easily reduced and it is possible that one of the construction materials in the APS-II system is reducing mercury and allowing it to be swept through the trapping medium as elemental mercury.

D.6 Potential Extensions of Colloidal Trapping

Many more metals than tested in this study also form hydrolysed hydroxides and could equally be recovered by this technique for analysis. The success in trapping arsenic also suggests that this technique may be effective for trapping other soluble polyacid anions such as hydrophosphate or hydrosulphate ions. These are of major importance in environment assessments and if trapping is efficient, this simple, universal hydrolysis trapping medium could readily replace the more expensive laboratory methods now used for routine analysis.

For more turbid water sources than those assessed in this study, the trapping medium could be modified to retain particulates by the straining mechanism. This would permit the analysis of trace levels of metal pollutants from high water volumes because the straining mechanism optimizes the permeability of the trapping bed. At the same time the chemical trapping would continue to immobilize the heavy metal hydroxides.

Finally, further work could be carried out to determine the optimum working surface of pumps, trap chambers and piping in the APS-II system. The performance of the present system is encouraging but the loss of mercury indicates that there is room for improvement.

E. CONCLUSIONS

A rapid, reliable and real time, on-line monitoring device is of paramount importance for emergency and real-time evaluation of toxic heavy metal concentration in surface water and waste-water.

For these purposes, a physical/chemical filter trapping system was established and tested in bench scale studies and used in an Automatic Preconcentration System (APS) study. The trapping system showed a good heavy metal retention capability at or above the part per trillion concentration level. It also has the filtration flexibility for high turbidity, large volumes and high flow rates in water sampling.

Additional work with more target heavy metals, with mononuclear oxyanions, and with optimizing working surface of pump, trap chamber and piping in the APS system may further improve and widen its applications.

Table 1
FILTER MEDIA PERFORMANCE

Run #	Filter Media*	Turbidity (NTU)		Pressure psi	Volume (Litre)
		Influent	Effluent		
1	W-934-AH 1.5um	0.15	0.13	20	10.0 ±0.5
2	Cambridge 1.0u	0.15	0.13	20	40.0 ±1.5
3	Cambridge 1.0u	5.00	2.00	20	10.0 ±0.2
4	Celite	0.15	0.10	5	100.0 *
5	Cellulose Purple Powder	5.00	0.60	14	1.0 ±0.0
6	Silica Gel	5.00	0.87	14	1.0 ±0.0
7	Sephadex Gel	5.00	0.81	14	1.0 ±0.0
8	Florisil	5.00	0.57	14	3.0 ±0.1
9	Activated Carbon	5.00	1.45	14	10.0 ±0.5
10	Granular Activated Carbon	5.00	0.96	14	2.0 ±0.0
11	Celite	5.00	0.41	14	25.0 ±1.5

Note: 1-4 Tests were carried out with filtration mode of Pumping. The rest were tested under suction mode(APS).
Two grams of filtration medium was used.

* Test was stopped deliberately.

TABLE 2

The effect of Celite Particle Size on the Filtration Efficiency

Turbidity of Input Water - 5 NTU
Filtration Mode: Suction (APS II)

Particle Size (μm)	TOTAL LITRES OF WATER RUN	FINAL PRESSURE INCH Hg	FINAL NTU
Whole Celite	25.0 $\pm$ 1.0	14	0.70
44 - 88	20.0 $\pm$ 0.8	14	0.68
D<44	8.0 $\pm$ 0.2	14	0.45
D>44	7.0 $\pm$ 0.2	14	0.31

Filter: Two gram celite supported with 1 μm pore size cambridge paper.

TABLE 3.

A Comparison Between the Pumping and the Suction Mode of Filtration
(INPUT WATER - 5 NTU)

	TOTAL LITRES OF WATER RUN	FINAL PRESSURE PSI
SUCTION	25.5 $\pm$ 1.0	14
PUMP	55.0 $\pm$ 2.0	25

Note: A vacuum gauger was used in suction system(APS II), which is in the unit of inch Hg. A pressure meter is used for pumping system, which is in the unit of psi.

Table 4

The Filtration Efficiency of Celite with Various Amount

Amount of Celite in Filter	Height cm	Effluent Final NTU	Final Pressure psi	Lites of Water Run
2 g	1.2	0.70	25	25.0 $\pm$ 0.5
5 g	2.4	0.46	25	34.5 $\pm$ 1.0
10 g	3.0	0.71	25	35.5 $\pm$ 1.0
15 g	3.7	0.54	25	31.0 $\pm$ 1.4
20 g	5.5	0.33	25	27.4 $\pm$ 1.0

Note: Turbidity of Input - 10 NTU; Filtration Mode: Pumping.

Table 5

Effect of Acid-Washed and Non-washed Celite
in Filtration Efficiency

Celite/Items	Total Litres of Water Passed	Final NTU
Acid-washed	53.0 $\pm$ 1.5	0.43
Non-washed	55.5 $\pm$ 1.5	0.18

Note: Filtration Mode - Suction; 2 grams Celite used; Tests
ended at 14 psi; Input Water 5 NTU; Flow Rate 100ml/min..

Table 6

The Effect of the Porosity of the Back-up Filter Paper
on the Quality and the Volume of Filtered Water

Filter	Litres of Water Run	Output NTU Start-End
Celite+cambridge	25 $\pm$ 0.5	0.68-0.32
Celite+Cambridge +Membrane	12 $\pm$ 0.5	0.47-0.18

Filtration Mode: Suction. 2 g Celite used Tests ended at
14 psi. Input Water 5 NTU. Flow Rate 100 ml/min..

Table 7

Concentration of Heavy Metals from the Extract of
Pre-washed Celite

Metals	Concentrations (ppb)		
	Blank	2% Nitric Acid	5% Nitric Acid
Pb	0.2 $\pm$ 0.0	1.0 $\pm$ 0.2	1.4 $\pm$ 0.4
As	ND	0.0	0.2 $\pm$ 0.0
Cd	0.1 $\pm$ 0.0	0.2 $\pm$ 0.0	0.3 $\pm$ 0.0
Hg	ND	0.0	0.0
Cu	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	0.4 $\pm$ 0.1
Cr	ND	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0

ND: Not Detectable.

Table 8
The Effect of Celite Matrix in Heavy Metal Retention

Matrix of Hydroxide	pH	% of Metal Ions Trapped in the Filter					
		Pb	Cd	As	Cr	Cu	Hg
Mg+ Celite	8	80.1 ±1.3	77.0 ±1.7	28.6 ±1.1	34.7 ±0.8	34.4 ±1.0	78.7 ±1.5
	9	89.7 ±1.8	80.7 ±1.6	15.0 ±0.4	32.0 ±0.8	40.0 ±1.1	73.0 ±1.3
	10	92.6 ±2.2	97.3 ±2.4	21.3 ±0.4	33.8 ±0.6	42.1 ±1.0	79.0 ±1.8
	11	90.7 ±2.1	98.0 ±2.6	52.7 ±1.0	20.0 ±0.7	64.3 ±1.1	83.3 ±1.4
Fe+ Celite	8	85.6 ±1.9	86.3 ±2.1	92.3 ±3.1	27.3 ±0.8	50.0 ±1.4	74.3 ±1.3
	9	92.0 ±2.2	90.3 ±2.2	59.7 ±1.1	24.0 ±0.4	55.3 ±1.1	76.0 ±1.7
	10	92.0 ±2.4	98.0 ±2.1	73.3 ±1.9	26.7 ±0.6	57.3 ±0.9	72.0 ±1.5
	11	91.3 ±2.4	98.0 ±2.4	65.3 ±1.5	21.1 ±0.8	56.0 ±1.0	76.3 ±1.5
Al+ Celite	8	75.5 ±1.5	61.7 ±1.4	76.5 ±1.0	17.3 ±0.6	23.0 ±0.4	64.6 ±1.4
	9	86.8 ±1.6	82.7 ±1.8	59.0 ±1.2	30.0 ±0.9	47.0 ±0.5	63.6 ±1.2
	10	93.7 ±2.1	97.7 ±2.3	50.0 ±1.1	40.0 ±0.8	98.5 ±2.6	72.3 ±1.4
	11	95.0 ±2.2	98.6 ±2.3	76.9 ±1.4	26.0 ±0.8	96.5 ±2.3	86.3 ±1.9
Celite only	8	61.4 ±1.3	54.6 ±1.5	18.9 ±0.6	14.8 ±0.4	34.5 ±1.3	48.7 ±1.2
	9	60.9 ±0.9	53.4 ±1.6	23.6 ±0.8	15.6 ±0.4	37.8 ±1.0	56.3 ±1.1
	10	62.7 ±0.9	51.5 ±0.9	23.8 ±0.8	14.9 ±0.3	38.6 ±1.4	57.6 ±1.2
	11	63.8 ±1.4	57.3 ±1.4	43.7 ±1.4	16.3 ±0.5	73.4 ±1.6	78.4 ±1.8

Note: 1 litre of ultrapure water spiked to 30 ppb with standard metal mixture. Ratio of metal to Celite: 0.2 mmole/gram. Filter: 5 gram Celite and cambridge filter paper.

Table 9
Effect of Coated Celite on Heavy Metal Retention
with Various Amount of Aluminum hydroxide

Metals	Percentage of HM's Trapped by the Matrix		
	0.1mmol/g	0.2mmol/g	0.3mmol/g
Cu	87.3 ±1.8	96.5 ±2.3	92.7 ±2.3
Hg	56.0 ±1.0	86.3 ±1.9	76.9 ±1.1
As	36.7 ±1.0	76.9 ±1.4	80.9 ±1.4
Cr	24.0 ±0.7	26.0 ±0.8	20.6 ±1.8
Pb	88.0 ±1.7	95.0 ±2.2	95.3 ±2.3
Cd	95.7 ±2.1	98.6 ±2.3	100.0 ±2.9

Note: Filter was made with five gram celite plus cambridge paper.
 The pH of spike ultrapure water(15ppb) was adjusted to 11.

Table 10

Percentage of Metal Ions Trapped on the Filter
Under Various Conditions

Sample: Spiked Ultrapure Water

pH	Pb	Cr	Cd	Cu	Hg	As
6	28.5±1.1	5.0±0.3	33.0±0.9	0.0	45.0±1.0	88.0±1.8
7	50.5±1.8	15.0±0.2	34.5±1.1	0.0	33.0±0.8	53.5±1.2
8	75.5±1.5	17.3±0.6	61.7±1.4	23.0±0.4	64.6±1.4	76.5±1.0
9	66.8±1.6	33.0±0.9	82.7±1.8	47.0±0.5	63.7±1.2	59.0±1.2
10	93.7±2.1	40.0±0.8	97.7±2.3	98.5±2.4	72.3±1.4	50.0±1.1
11	95.0±2.2	26.0±0.8	98.6±2.3	96.5±2.3	86.3±1.9	76.9±1.4
12	96.0±1.2	0.0	96.5±2.2	70.5±1.3	99.0±2.8	56.0±1.0

Sample: spiked ultrapure water 30 ppb for each metal.

Table 11

Bench Scale Study

Percentage of Metal Ions Trapped on the Filter
Under Various Conditions

Sample: Spiked Rideau River Water (R.R.W) One Litre

pH	Pb	Cr	Cd	Cu	Hg	As
7	71.4±1.8	51.2±0.9	81.3±1.8	50.0±0.9	84.3±1.9	30.0±0.7
8	36.0±2.0	58.1±0.9	81.3±2.0	45.0±1.6	84.7±2.1	39.7±0.6
9	88.8±1.9	56.2±2.0	82.5±1.8	32.2±1.0	85.7±1.7	29.7±0.6
10	87.2±1.8	49.8±1.6	86.3±1.8	41.6±1.1	91.7±2.9	53.3±1.0
11	89.5±1.4	75.1±2.1	99.4±2.6	69.6±2.0	99.3±3.0	57.0±1.0
12	99.1±2.3	56.2±0.9	97.5±2.5	59.0±1.6	100±2.9	71.0±1.2
Spike(ppb)	30.0	30.0	30.0	30.0	30.0	30.0
RR Water	2.8 ±0.2	2.2 ±0.2	2.0 ±0.1	2.9 ±0.1	0.0	0.0

Sample: Rideau River Sample II. Filter: Celite coated with
aluminum hydroxide.

Table 12

Effect of Nitric Acid Volume on Extraction Efficiency
(Sample : Spiked Ultrapure Water)

Metals	Percentage of Recovery Rate		Total Recovery
	1st 100ml	2nd 100ml	
Pb	76.3 ± 1.2	19.3 ± 0.4	95.6 ± 1.6
Cr	13.0 ± 0.4	2.7 ± 0.0	15.7 ± 0.4
Cd	80.0 ± 1.5	15.3 ± 0.5	95.3 ± 2.0
Cu	71.3 ± 1.7	15.7 ± 0.4	87.0 ± 2.1
Hg	70.7 ± 2.0	15.0 ± 0.1	85.7 ± 2.1
As	63.0 ± 1.6	11.3 ± 0.2	74.3 ± 1.8

Note: Filter was made with five gram celite plus cambridge paper. One litre ultrapure water was spiked to 3.0 ppb.
Nitric Acid: 5%. Data are the average of two duplicates.

Table 13

Effect of Nitric Acid Volume on Extraction Efficiency
(Sample: Rideau River Water)

Metals	Percentage of Recovery Rate			Total Recovery
	1st 100ml	2nd 100ml	3rd 100ml	
Pb	67.7 ± 1.4	21.3 ± 0.4	6.0 ± 0.1	95.0 ± 1.9
Cr	48.3 ± 0.8	16.7 ± 0.2	8.0 ± 0.0	73.0 ± 1.0
Cd	69.7 ± 1.0	14.0 ± 0.1	5.7 ± 0.1	89.4 ± 1.2
Cu	50.7 ± 0.8	12.7 ± 0.1	5.0 ± 0.1	68.4 ± 1.0
Hg	72.7 ± 1.8	19.3 ± 0.2	4.7 ± 1.0	96.7 ± 2.1
As	51.0 ± 0.9	8.3 ± 0.1	0.0	59.3 ± 1.0

Note: Filter was made with five gram celite plus cambridge paper.
One litre Rideau River water was spiked to 3.0 ppb.
Nitric Acid: 5%. Data are the average of two duplicates.

Table 14

Spike Recovery of Heavy Metals from Reagent Water

Metals	Recovery Rate APS-II	Bench Scale Study
Lead	91.5 $\pm$ 1.9	95.6 $\pm$ 1.6
Chromium	33.0 $\pm$ 1.1	15.7 $\pm$ 0.4
Copper	107.0 $\pm$ 3.1	87.0 $\pm$ 2.1
Cadmium	92.5 $\pm$ 2.4	95.3 $\pm$ 2.0
Arsenic	8.5 $\pm$ 1.3	74.3 $\pm$ 1.8
Mercury	8.0 $\pm$ 1.2	85.7 $\pm$ 2.1

Test Run Of Inorganic APS-II Sampler, flow rate 100ml/min..

Sample: Spiked Ultrapure Water (100 ppt), total volume 15 litres.

Table 15

Spike Recovery of Heavy Metals from Rideau River Water

Metals	Recovery Rate APS-II	Bench Scale Study
Lead	91.0 $\pm$ 2.3	95.0 $\pm$ 1.9
Chromium	46.4 $\pm$ 1.2	73.0 $\pm$ 1.0
Copper	81.4 $\pm$ 1.9	68.4 $\pm$ 1.0
Cadmium	98.4 $\pm$ 3.0	89.4 $\pm$ 1.2
Arsenic	61.4 $\pm$ 1.6	59.3 $\pm$ 1.0
Mercury	6.4 $\pm$ 1.0	96.7 $\pm$ 2.1

Sample: Spiked Rideau River water(100ppt), total volume 10 litres.

Flow rate 100ml/min..

Fig. 2

The Effect of Celite Particle Size on the Filtration Efficiency

Fig. 3

Filtration Efficiency with Various Amount of Celite

Input: 10 NTU, Filtration Mode: Pumping

Fig. 4

Filtration Results with Various Amount of Celite

Final Pressure: 25 psi; Filtration Mode: Pumping.

■ 5.5CM (20 G) + 3CM (10 G) — 3.75CM (15 G) ▲ 2.45CM (5 g)

Fig. 5 Filtration Results
With Different Height of Filter Medium

Fig. 6

Plot of Input NTU vs Litres of Water Passed through the Filter

Final pressure: 25 psi; Filtration Mode: Pumping, 2 g Celite Used

Fig 7. Effect of Hydroxide Coating Celite in Heavy Metals' Retention

2 OF/DE 2

PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

Fig. 8 Effect of Aluminum Hydroxide Amount on Heavy Metal Trapping Capacity

Fig. 9 Recovery Rate of Heavy Metals
at Various pH with Spiked Reagent Water

Fig. 10

Recovery Rate of Heavy Metals at Various pH with Spiked River Water

Photography 1. Microstructure of Celite

**Photography 2. Celite Coated with
Aluminum Hydroxide**

**Photography 3. Celite Coated with Aluminum Hydroxide
through Which A Heavy Metal Solution Passed.**

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