

NWRI Contribution 88-65

DETERMINATION OF LOW LEVEL  
 $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  IN WATER  
BY ION CHROMATOGRAPHY

by  
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January 1988

## MANAGEMENT PERSPECTIVE

Cadmium is a toxic priority-element which has created a great deal of environmental attention and concern. Reliable low-level Cd data for environmental studies are not available due to lack of sensitive methods. A sensitive ion chromatographic method has been developed, which can simultaneously analyze Cd, Co and Mn down to 0.1 ppb level and which satisfies the various water quality guidelines and objectives. The method is completely automated and is a good complementary method to AA and ICP. The method was developed, at the request of the Water Quality Branch, as part of the Analytical Chemistry Research project for 1987/88.

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## PERSPECTIVE-GESTION

Le cadmium est un élément toxique prioritaire dont la présence dans l'environnement a suscité beaucoup d'intérêt et d'inquiétude. Il n'y a pas de données fiables sur les faibles concentrations de Cd dans l'environnement, car il n'existe pas de méthode assez sensible pour les mesurer. On a mis au point une méthode de chromatographie d'échange d'ions sensible, qui permet de doser simultanément le Cd, le Co et le Mn jusqu'à une concentration de 0,1 p.p. milliard, conforme aux divers objectifs et directives relatifs à la qualité de l'eau. Cette méthode est entièrement automatisée; elle complète bien la spectrométrie d'absorption et par émission de plasma (ICP); on l'a mise au point à la demande de la Direction de la qualité des eaux, dans le cadre du projet de recherche en chimie analytique de 1987-88.

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## ABSTRACT

An automated ion chromatographic method for analysis of low- and sub-ppb Cd in water preserved with 0.2% HNO<sub>3</sub> is described. The detection limit of 0.1 ppb satisfies the various guidelines and objectives of 0.2 ppb Cd. The method is also applicable to determination of Co and Mn down to 0.1 ppb. The automation, on-line concentration and simultaneous determination of the three elements is an advantage over the flame and furnace AA.

Key Words: ion chromatography, post-column chelation, trace cadmium, cobalt and manganese, automation

## RÉSUMÉ

On décrit une méthode de chromatographie d'échange d'ions automatisée servant au dosage du Cd à des teneurs de l'ordre de quelques parties par milliard ou moins dans de l'eau préservée par du  $\text{HNO}_3$  à 0,2 %. La limite de détection de 0,1 partie par milliard est conforme aux directives et objectifs relatifs à la qualité de l'eau (0,2 p.p. milliard). Cette méthode peut aussi servir au dosage du Co et du Mn, jusqu'à 0,1 p.p. milliard. Comme elle permet de doser simultanément ces trois éléments automatiquement et en direct, elle est plus avantageuse que la spectrométrie d'absorption à la flamme ou au four.

Mots clés : Chromatographie d'échange d'ions, chélation après échange, cadmium, cobalt et manganèse à l'état de traces, automatisation.

## 1.0 INTRODUCTION

Cadmium is a toxic priority-element which has created a great deal of attention and concern [1-4]. In trend and long-term monitoring studies, reliable low-level Cd data are not available due to lack of sensitive methods. Consequently, it has been recommended that sensitive and reliable methods be developed [2].

Routine analyses of trace metals including cadmium are commonly carried out using atomic absorption spectrometry (AA) and inductively coupled plasma (ICP) atomic emission spectrometry [5]. Lum and Callaghan [6] claimed to have validated a direct injection graphite furnace-AA method giving a <2 ppt detection limit. However, Sturgeon [7] recently pointed out some difficulties with direct trace analysis by graphite furnace and stated that direct quantitative determination of low-ppt Cd is not feasible without sample preconcentration.

Separate sample preconcentration is required by AA and ICP analysis of low levels [5]. Since ion chromatography (IC) technique is potentially cost-effective as recently shown for anions and cations [8], and is suitable for studying metals and their speciation [9], we decided first to test IC in investigating low-level Cd. It has been stated that a detection limit as low as 0.1 ppb Cd<sup>2+</sup> is attainable by IC [9] but Mn<sup>2+</sup> would coelute, which is unacceptable in water analysis. Recently, Rubin and Herberling [10] reported an IC method that separates Cd<sup>2+</sup> and Mn<sup>2+</sup>, but it is not very sensitive for sub-ppb Cd<sup>2+</sup>.

In this study, we concentrated on developing an IC method which not only can separate Mn<sup>2+</sup> from Cd<sup>2+</sup> but also can detect Cadmium down to 0.2 ppb limit as required by various guidelines and objectives (Table 1). As will be shown low- and sub-ppb Cd<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup> can be simultaneously determined with recoveries ranging from 95 to 107% in 20 out of 21 attempted recoveries.

## 2.0 EXPERIMENTAL

### 2.1 Chemicals

Very high purity chemicals were used: Acetic acid, Seastar Chemicals and Merck 739055 Suprapur; Oxalic acid·2H<sub>2</sub>O, Fluka 75700; Lithium hydroxide·H<sub>2</sub>O, Fluka 62530; Pyridine-2, 6-dicarboxylic acid (PDCA), Fluka 82790; HNO<sub>3</sub>, Seastar Chemicals and Baker Instra-analyzed; 4-(2-Pyridylazo) resorcinol (PAR), Fluka 83970; NH<sub>4</sub>OH, Seastar Chemicals and Merck 010983 suprapur; NaCl, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COONa, Merck suprapur; 2-Dimethylaminoethanol (DMAE), Fluka 38990, Aldrich D15,740-6; Metal standard stocks, Fisher Scientific Company. Milli-Q Water (18M $\Omega$ ) was used. Labware was cleaned with 30% HNO<sub>3</sub> [11].

### 2.2 Equipment and Operation Conditions

The system comprises a Dionex chromatograph 2000 (with an analytical pump, a reagent delivery module and a membrane reactor), a Kratos visible spectrophotometric detector (Spectroflow 757), an HP 3390 recorder-integrator, a Technicon auto sampler IV, two loading pumps (Dionex DQP-1) and an Auto Ion 100 for automation.

Figure 1 shows the system schematic and valve configuration for sample concentration, rinsing and injection. A typical run starts with sample loading via valve I INJECT, sample flushing via port 5 of valve II to flush out any carryover, and sample concentrating via ports 7 of valves II and III into the concentrator column CG3 (the right one) and to waste. The run continues with sample rinsing by MQ water (18 M $\Omega$ , stripped of trace metals by CG5 column, via valve I LOAD), followed by sample injection via valve III INJECT. The analyte metals are separated by CS5 column, and in the reaction chamber react with PAR to form metal chelates, which are detected and measured at 520 nm. The operating conditions are summarized in Table 2. Calibration curves and one-point calibrations were used.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Chelate Formation

The chelating reagent 4-(2-pyridylazo) resorcinol (PAR) is known to be a very sensitive reagent for spectrophotometric determination of metals. For example, it has been successfully used in spectrophotometric studies of trace cadmium and vanadium [12 - 15]. PAR is used here for post-column chelating  $\text{Cd}^{2+}$  eluted from the cation exchange column CS5 as labile  $\text{Cd-PDCA}_n$  complexes. The stable chelate is most likely  $\text{Cd}\cdot\text{PAR}_2$  [16], perhaps formed by the following reaction:



and is measured at 520 nm.

#### 3.2 Choice of Eluants and Post-Column Reactants

Oxalic acid eluant was found to give very good sensitivity for  $\text{Cd}^{2+}$  determination but was incapable of separating  $\text{Cd}^{2+}$  from  $\text{Mn}^{2+}$ . It is therefore unsuitable in any water analysis of metals.

Pyridine-2, 6-dicarboxylic acid (PDCA) was found to be capable of separating  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  but several variations and combinations of eluant/post-column reactant had to be tested for desired sensitivity. The chemicals for various eluants were PDCA, LiOH, NaCl,  $\text{CH}_3\text{COONa}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{Na}_2\text{SO}_4$ . Those for various post-column reactants were PAR,  $\text{NH}_4\text{OH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and DMAE (dimethyl aminoethanol). The combination giving optimum sensitivity and reproducibility for  $\text{Cd}^{2+}$  was  $(\text{PDCA} + \text{LiOH} + \text{Na}_2\text{SO}_4 + \text{NaCl}) / (\text{PAR} + \text{NH}_4\text{OH} + \text{DMAE})$ , as detailed in Table 2.



### 3.3 Enrichment Process

On-line enrichment was necessary to achieve sub-ppb  $\text{Cd}^{2+}$  level. The sample is loaded and concentrated on CG3 in valve III OFF after the system has been flushed with same sample to avoid carryover (Fig. 1 and Table 2). It was found that 10 ml of sample was enough to attain the desired sensitivity.

The enrichment process reveals that the background contamination can be serious for several metals, most notably  $\text{Zn}^{2+}$ , giving variable baseline peaks. For ultra-trace works, a class 100 type environment is required to avoid this type of contamination. Our laboratory is not one such environment. Nevertheless, for sub-ppb  $\text{Cd}^{2+}$  and in this case sub-ppb  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  also, the background contamination is not a problem as we get consistently clean baselines.

### 3.4 Effect of Sample Acidity

Unacidified natural or standard samples are easy to analyze, giving well-defined chromatograms, but are in practice useless due to metal loss with storage time. Our common practice is to preserve water samples with 0.2%  $\text{HNO}_3$ (v/v). But this acidity could elute  $\text{Cd}^{2+}$  from CG3 concentration column and prevent concentration process. Thus an acidity effect was studied on  $\text{Cd}^{2+}$  along with  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ , and plotted in Figure 2. It can be seen that the metals are well-retained at 0.2% and 0.5%  $\text{HNO}_3$ , but at 1.0% the acid starts acting as eluant, noticeably for  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ .

The 0.2% acidity, however, upsets the behaviour of chromatograms, giving rise to negative dip at the early part of the elution pattern. Coupled with the background contamination mentioned above, the early peaks are a problem. Fortunately, this effect does not significantly upset the  $\text{Cd}^{2+}$  peak; in fact, a rinse of CG3 with 3 ml of Milli-Q water ensures sensitive and reproducible  $\text{Cd}^{2+}$  peaks to meet our objective of 0.2 ppb capability (Table 1). Furthermore, under these

conditions  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  peaks were also more reproducible than other metals, and thus were included in this study (Fig. 3). Rinsings with very dilute carbonate solutions, instead of water, were also tested but showed no advantages.

### 3.5 Interferences

As discussed above, the hydronium ion is an interferent at 1% concentration (pH 0.8). The concentration at which the ion starts interfering lies between 0.5 - 1.0 %, which is well above our normal use of 0.2%.

$\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  concentrations are often higher than  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  in waters and can become concentration interferents if present at much higher concentrations. However, 100 ppb  $\text{Zn}^{2+}$  and 100 ppb  $\text{Mn}^{2+}$  do not interfere with analysis of 0.5 ppb  $\text{Co}^{2+}$  and 0.5 ppb  $\text{Cd}^{2+}$ . Three hundred (300 ppb)  $\text{Al}^{3+}$  was also tested but proved to be a non-interfering species. In general, if the analytes are present in minute quantity relative of other metals eluting nearby, the concentration interferences can be a problem. This can, however, be solved by properly managing the waste solution from the detector. By identifying and discarding the interfering-fraction of the solution, one collects and re-analyzes the analyte-containing fraction.

### 3.6 Performance Characteristics

#### 3.6.1 Standard reference materials

A Standard Reference Material, SRM 1643b: trace metals in water, of the National Bureau of Standards was used. The material containing 0.5 M  $\text{HNO}_3$  had to be diluted to our normal working acid content of 0.2%  $\text{HNO}_3$ . The results found agree well with the certified values, taking dilution into account (Table 3). Two spikes were also added to the diluted material and the recoveries satisfactorily made (Table 4). Calibration curves were used, one of which is shown in Figure 4.

### 3.6.2 Quality control samples

Two samples, regularly used in our interlaboratory quality assurance (QA) programs, were tested. The first quality control sample, TM201, was prepared using Lake Ontario water for direct aspiration atomic absorption technique (high levels) and for solvent extraction technique after proper dilution (low levels).

The sample was diluted 200 times, reacidified to 0.2% HNO<sub>3</sub>, and analyzed. The results found are in good agreement with the design values, which are the multi-laboratory and multi-study averages (Table 5).

The second sample, synthetic rain A, which was specifically prepared for an acid rain-related QA program (the Long Range Transport of Airborne Pollutants, LRTAP) was tested for the three metals. The results compared well with the median of 33 interlaboratory results (Table 5) [17].

### 3.6.3 Precipitation samples

Two precipitation samples preserved with 0.2% HNO<sub>3</sub> was analyzed for, and then spiked respectively with Co<sup>2+</sup>, Cd<sup>2+</sup> and Mn<sup>2+</sup> as follows: 0.5, 0.5 and 2.0 ppb for Quebec sample; 0.5, 0.5 and 1.5 ppb for British Columbia (B.C.) sample. Table 6 shows satisfactory recoveries and precision.

### 3.6.4 Analytical range

The detection limits under the given conditions are 0.1 ppb for each of the three elements and compare favourably with the revised detection limits of the atomic absorption solvent-extraction methods of 0.5, 0.1 and 1.0 ppb [5] and those of the interlaboratory "specification" studies of 2.0, 1.0, 2.0 [18] for Co<sup>2+</sup>, Cd<sup>2+</sup>, and Mn<sup>2+</sup>, respectively.

As this work centers around low- and sub-ppb analyses, the upper limit was not studied. This limit, however, should be quite high since concentrated samples can be easily dealt with by decreasing the concentrating volume and/or by sample dilution.

### 3.7 Advantages and Disadvantages

The automation, on-line concentration and simultaneous determination is a definite advantage over the flame and graphite atomic absorption spectrometry. If lower detection limit is required, one simply on-line concentrates more than 10 ml sample. For AA and ICP on the other hand, routine analysis of low-level metals first requires separate preconcentration of 100 ml sample by solvent extraction or evaporation technique. The IC is also relatively cheap to operate.

Although it is a good complementary method to AA and ICP, the somewhat slow analysis time of IC would be a disadvantage in routine use when compared to ICP.

### 4.0 CONCLUSIONS

A sensitive ion chromatographic method has been developed for simultaneous determination of low- and sub-ppb  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  in dilute water samples. It is fully automated and is a good complementary method to AA and ICP.

**ACKNOWLEDGEMENT**

Mr. E. Xue Li thanks Mr. A.S.Y. Chau for the arrangement and development of a training program for his visit at NWRI and is grateful to WHO for the financial support in the form of a visiting fellowship.

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TABLE 1

Various Water Quality Guidelines and Objectives

(concentration permissible,  $\mu\text{g Cd/L}$ )

Water Type	GLWQ* Agreement (1987)	US EPA** WQ Criteria (1973 & 1980)	IJC - GLWQ*** Objectives	Canadian**** WQ Guidelines (1987)
Drinking Water Supply/Ambient Water	-	10	-	5
Freshwater Aquatic Life	0.2	1.5 (in soft water) 6.3 (in very hard water)	0.2	0.2 (in soft water) 1.8 (in very hard water)
Irrigation Water	-	10	-	10

\* "Great Lakes Water Quality Agreement of 1978" (Revised November 1987),  
International Joint Commission, Ottawa, 1978, Annex 1, p.3

\*\* United States Environmental Protection Agency Water Quality Criteria [4a]

\*\*\* International Joint Commission - Great Lakes Water Quality Objectives [4a]

\*\*\*\*Canadian Water Quality Guidelines [4b]

TABLE 2

Operation Conditions

		Sample Handling			Eluant (ml/min)	Concentrator	Separator	Detection	
		Flushing	Loading	Rinsing				Injection	Post-Column Chamber
4 mL	10 ml	3 ml			3mM PDCA	HPIC-CG3 (50 x 4 mm)	HPIC-CS5 (250 x 4mm)	0.2 mM PAR	520 nm
Valve I ON	Valve I ON	Valve I OFF	Valve I ON		4.3mM LiOH			0.5 M NH <sub>4</sub> OH	.1(.05)AUF5
Valve II OFF	Valve II ON	Valve II ON	Valve II OFF		2mM Na <sub>2</sub> SO <sub>4</sub>			1.0 M DMAE	
Valve III OFF	Valve III OFF	Valve III OFF	Valve III ON		25mM NaCl (1.0 ml/min)			(0.6 ml/min through membrane reactor)	



/ / LOAD, OFF  
 / / INJECT, ON

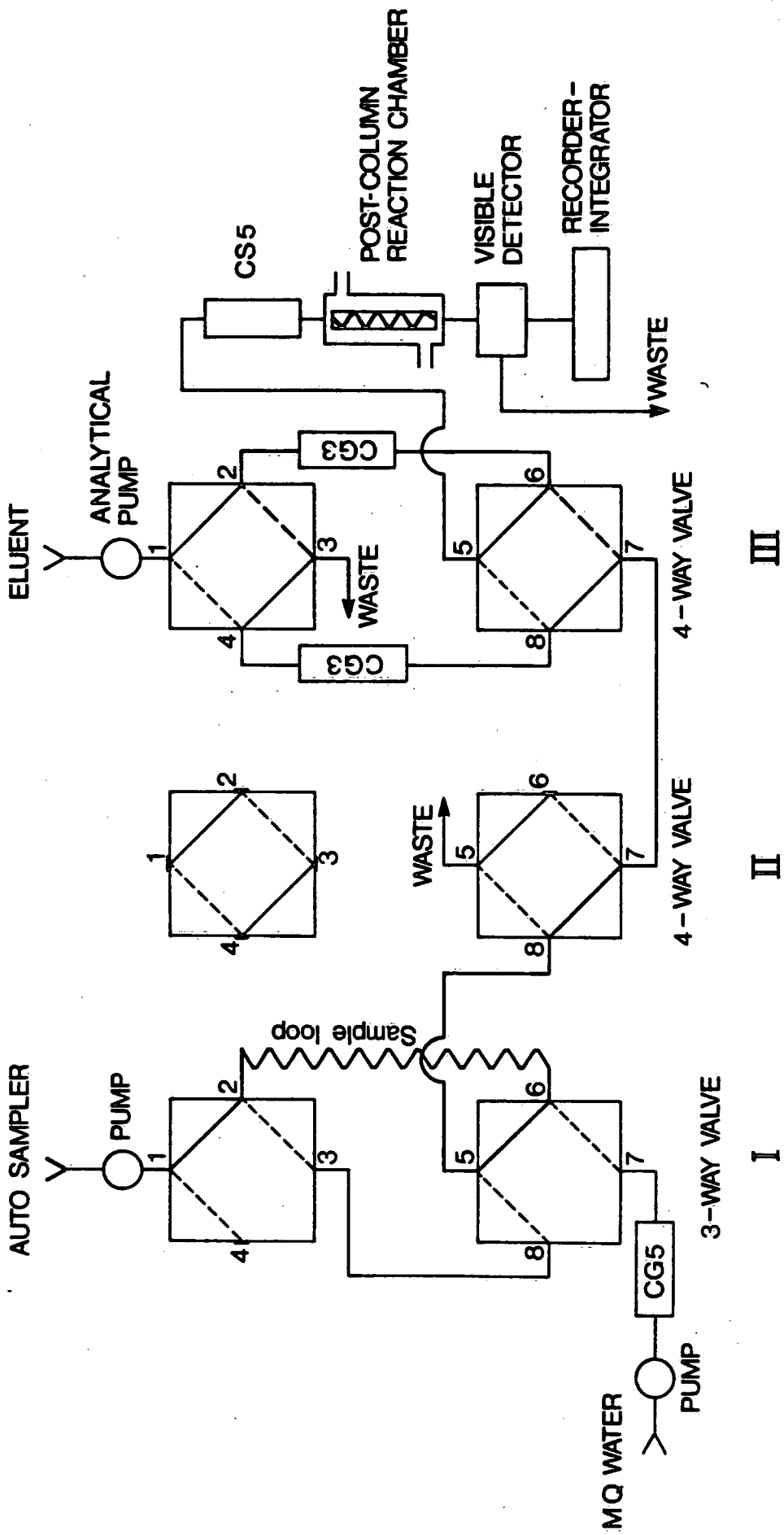


Figure 1. Valve positioning for sample enrichment and injection, and system schematic

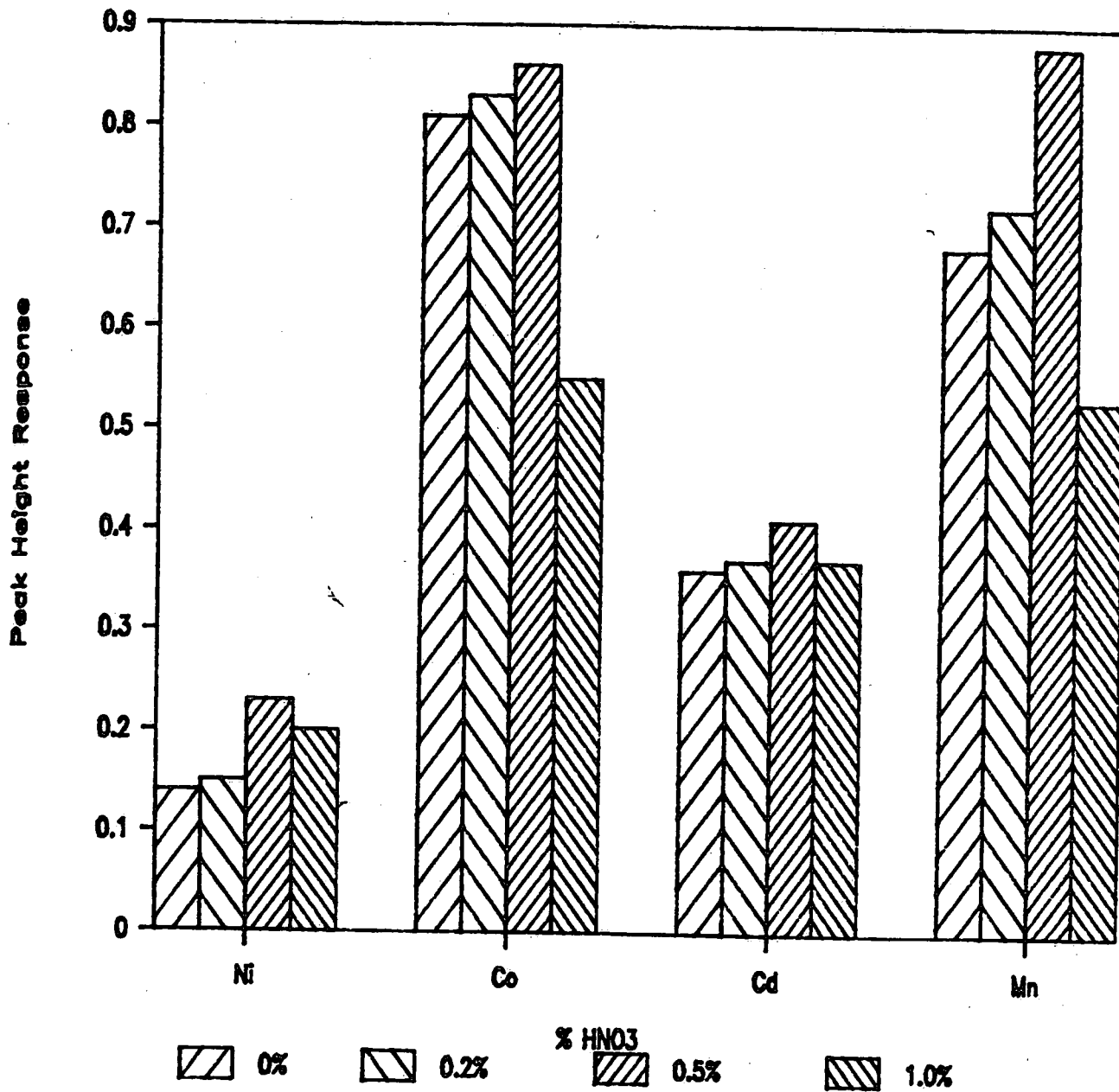


Figure 2. Acid effect on response of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$

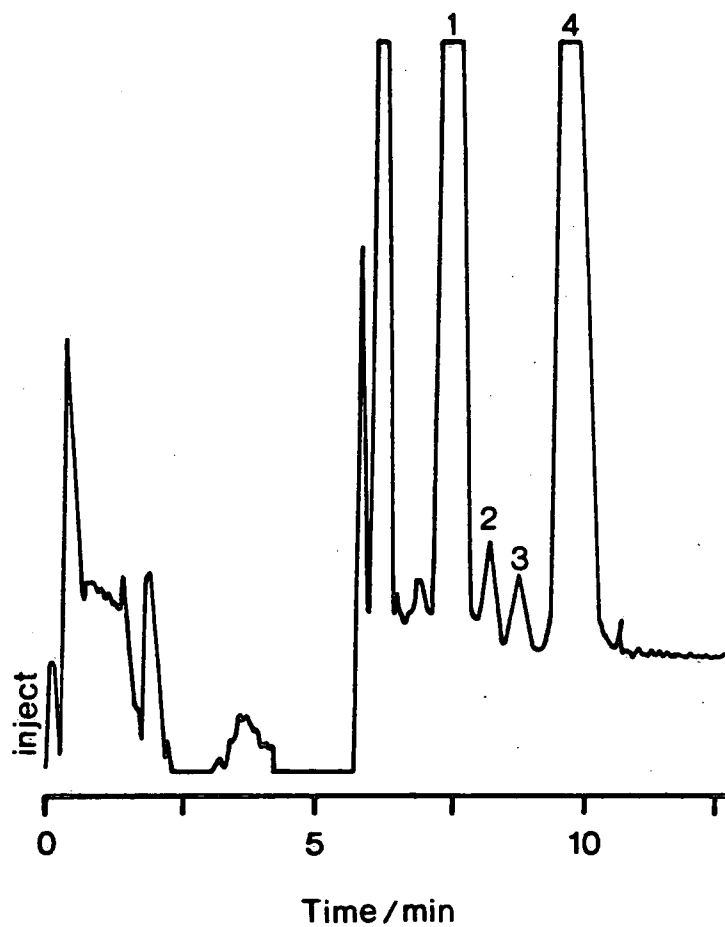


FIGURE 3 Chromatogram of a spiked precipitation sample from Québec:  
1  $\text{Zn}^{2+}$ , ~60ppb; 2  $\text{Co}^{2+}$ , 0.53ppb;  
3  $\text{Cd}^{2+}$ , 0.87ppb; 4  $\text{Mn}^{2+}$ , 9.39ppb  
Conditions given in Table 1

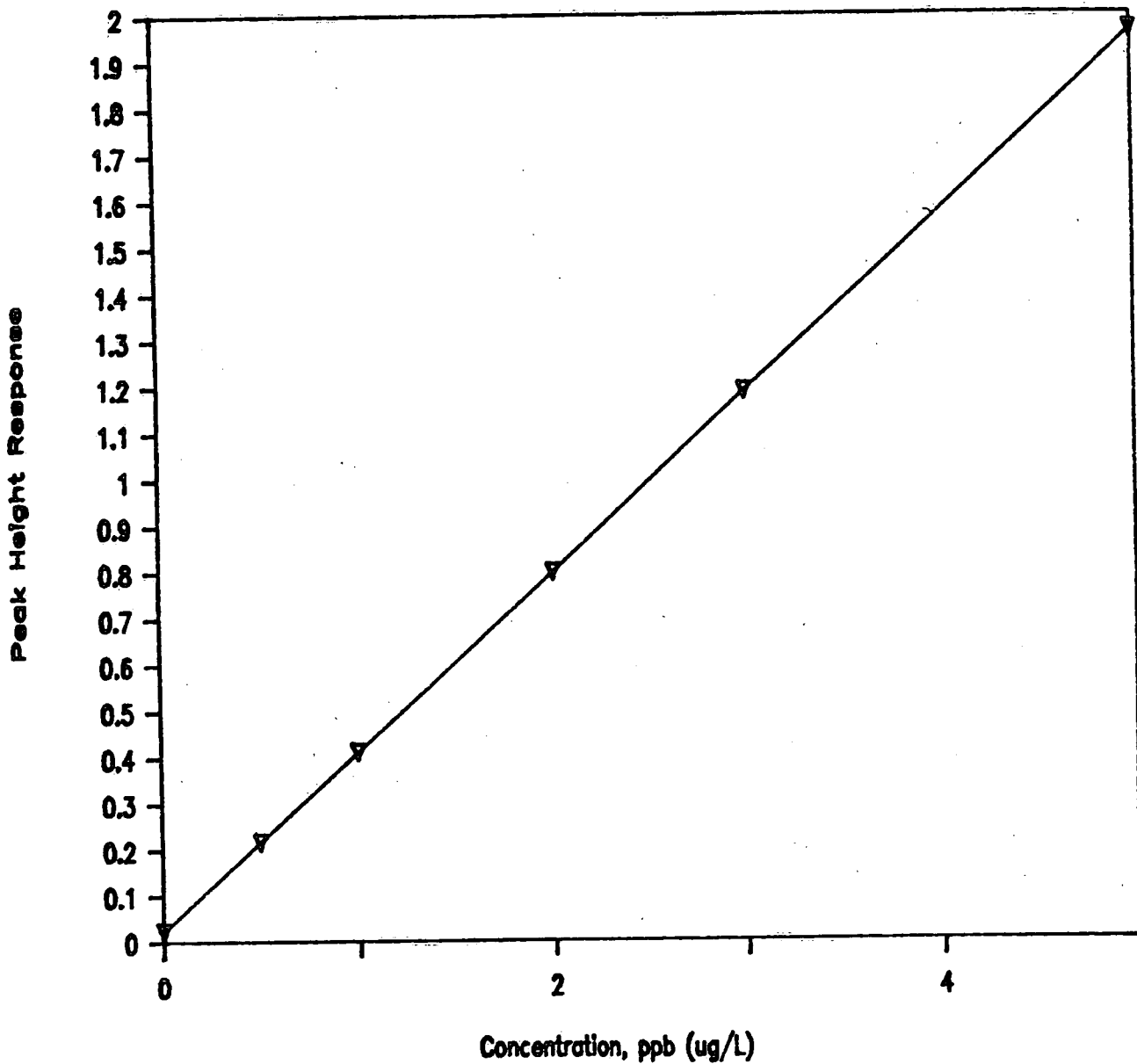


Figure 4. Cd<sup>2+</sup> calibration curve