

Study On Simultaneous Determination of Ni, Pb and Cd by Ion Chromatography

P.F. Gao*, X.W. Zhang, H.Z. Kuang, Q.Q.Li, Y. Li

College of Environmental Science and Engineering, Xiamen University of Technology, Xiamen 361024, China.

gaopf@xmut.edu.cn

Abstract. In this paper, a ion chromatographic method was established for simultaneously determining three toxic heavy metal ions(Ni^{2+} , Pb^{2+} , Cd^{2+}) . the optimal chromatographic conditions are using a conductivity detector, with the Metrosep C₄ column was used, the mixture of 0.07mmol/L nitric acid and 0.5mmol/L dipicolinic acid as eluent, the flow rate was 0.25 mL/min. Three kinds of heavy metals all showed satisfying linear relationships, and the correlation coefficients ranged from 0.9979 to 0.9994. the detection limits were in the range of 0.01-0.05 mg/L. The method is an easy, accurate and reliable way to assess soil heavy metal pollution.

1. Introduction

As one kind of persistent pollutants, the heavy metals are considered as main contaminations in the environment due to their toxicity and ability to accumulate (Khan 2015). The determination of heavy metal content in soil is gradually obtaining attention by people along with the development of economy and industry (Stasinis 2013, Al-Khashman 2018).

The detection mode include traditional chemical analysis methods and instrumental analysis methods. Traditional chemical methods do not require expensive and sophisticated equipment, but their operation procedures are often not convenient and efficient enough. Just like complexometric titration method or spectrophotometry. Some instrumental analytical techniques are suitable for the measurement of heavy metal ion, such as flame atomic absorption spectrometry (Omidi 2015, Leśniewska 2016), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Kos 1996, Wang 2017), inductively coupled plasma mass spectrometry (ICP-MS) (Hussain 2017), laser atomic fluorescence spectrometry and total reflection X-ray fluorescence (TXRF) (Macedomiranda 2009) and so on. These methods have some advantages, such as high sensitivity, lack of chemical interferences, low detection limits, and are suitable for determining trace elements. But these measurement methods require high testing costs, expensive and sophisticated apparatuses and professional technical staff, and primary laboratory can not meet these requirements.

Relative to the two kinds of methods mentioned above, Ion chromatography is a rapid, highly selective and sensitive method, which will be widely used in Environmental Analysis(Moutaz 2015, Bruno 2006, Liu 2010), its hardware cost of equipment devices are moderate. The running costs of this method are also not expensive.

Therefore, the aim of this paper is to develop a rapid and high effective method for the determination of heavy metal ion, and applied in the assessment of soil heavy metal pollution.



2. Methods and materials

2.1. Chemicals

All reagents were analytical grade. Individual pure standards containing 1,000 mg L⁻¹ of trace metals in 0.5 normal nitric acid (Ni, Cd, Cr, Pb, Cu, Zn, As, Na, K, Ca, Mg and Mn), hydrochloric acid and nitric acid were purchased from National drug group chemical reagents Co., Ltd. 2,6-Pyridinedicarboxylic acid was purchased from Sigma-Aldrich. Ultrapure water was got with a Milli-Q system (Millipore, USA).

2.2. Instrumentation

Heavy metal ion were analyzed ion-chromatography (Metrohm, 883 Basic IC plus) with Metrohm Metrosep C4-150/4.0 column and with nitric acid-2,6-Pyridinedicarboxylic acid as eluent.

A closed-vessel microwave digestion method is used for soil samples dissolution with Anton-parr Mutilwave 3000. 0.5 g soil sample was decomposed with HNO₃ acid in a PTFE digestion vessel by using microwave heating for 5 min at 500 W of microwave power. Then the digestion solution was diluted to 25 mL and filtrated by 0.45µm micropore filter.

3. Results and discussion

3.1 Optimization of Separation Conditions

The chromatographic behaviour of several heavy metal ions with different eluents was studied. Only the detection peaks of four heavy metal ions were observed, including Ni, Pb, Cd and Mn, when the composition of the mobile phase was 0.07 mM HNO₃ and 0.5mM 2,6-Pyridinedicarboxylic acid. As was show in the Table 1.

Table 1. The conditions of ion peak under the different eluents

HNO ₃ +2,6-Pyridinedicarboxylic acid	Ni	Pb	Cd	Mn
0.13 mM-0.9mM	-	-	+	+
0.13 mM-0.7mM	-	+	+	+
0.07 mM-0.9mM	-	-	+	+
0.07 mM-0.7mM	-	+	+	-
0.07 mM-0.5mM	+	+	+	+
0.07 mM-0.3mM	+	-	+	-

Note: the plus sign means its peak was observed and negative sign showed no peak.

The effect on the separation result were investigated with different flow rate of eluent. The results was shown in Table 2. Finally, a good separation was obtained at 0.25 mL/min flow-rate, it is shown in Fig. 1. No peak overlap was found. However, the peak time of manganese takes more than 20 min, and it is not selected as the detected object.

Table 2. Retention time varies with changes in the flow rate of the mobile phase

Current Speed	Ni	Pb	Cd	Mn
0.4mL/min	3.6min	5.1min	5.1min	29.2min
0.25mL/min	5.2min	8.2min	8.9min	32.1min

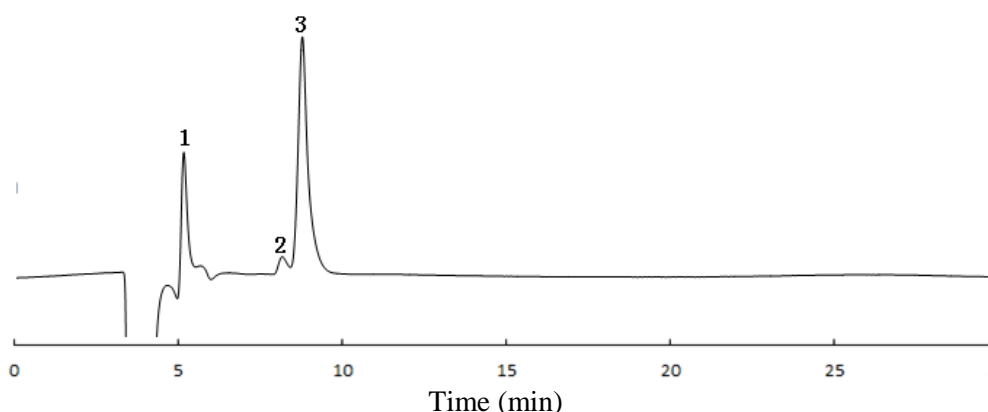


Figure 1. Chromatogram of three metallic ions(1.Ni²⁺, 2. Pb²⁺, 3.Cd²⁺)

3.2 Effects of common alkali metal ions and alkaline earth metal ions in soil

It is generally known that Na⁺ and K⁺ are the common alkali metal ions in soil, and Ca²⁺ and Mg²⁺ are the commonly coexist alkaline-earth metal ions. The influence of Na⁺, K⁺, Ca²⁺ and Mg²⁺ on the heavy metallic ions was investigated. Under the optimized separation conditions, the peak times of Common cation ion(K⁺, Na⁺, Ca²⁺, Mg²⁺) more that 30 minutes, and the retention times of Ni²⁺, Pb²⁺ and Cd²⁺ were not disturbed by the coexist alkali metal ions and alkaline earth metal ions. At the same time, the peak areas of three heavy metallic ions were investigated with four kinds of concentrations Na⁺, K⁺, Ca²⁺ and Mg²⁺. The four kinds of concentrations are respectively 5mg/L, 10mg/L, 15mg/L, 20mg/L.

As was shown in Fig.2 to Fig.5, the peak areas of Pb²⁺ and Cd²⁺ were not influenced by the alkali and alkaline-earth metals variations, and the peak area of Ni²⁺ was not observed when K⁺ concentration was more than 10mg/L. The same phenomenons occurred when the coexisting ions were Na⁺, Ca²⁺ or Mg²⁺. In general, the concentrations of K⁺, Na⁺, Ca²⁺, Mg²⁺ were 0.1g/kg in the acid soils of southern China(Wang, 2008). their concentrations were less than 2mg/L in the soil sample solutions according the preceding pretreatment method. Therefore, there is no interference in the determination of Ni²⁺ in the practical application with the existence of K⁺, Na⁺, Ca²⁺ or Mg²⁺.

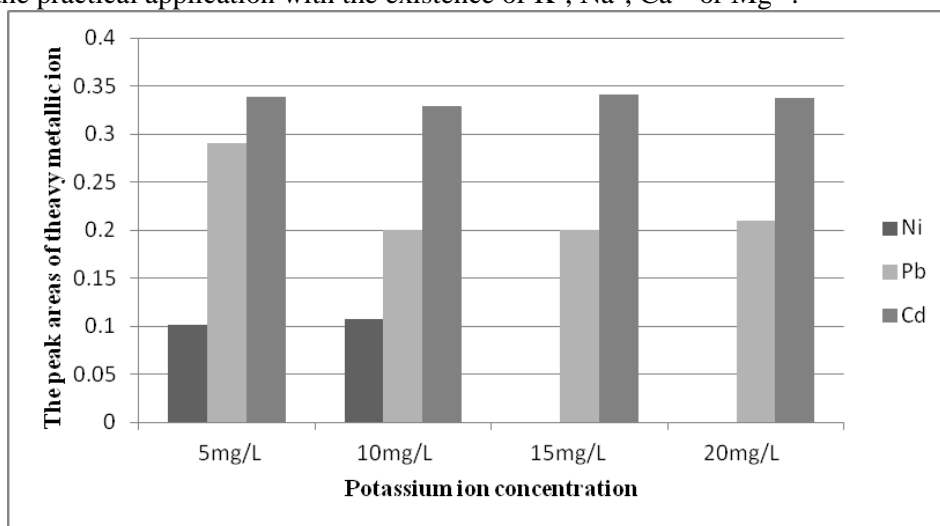


Figure 2. Influence of different K⁺ concentrations on the peak area of heavy metallic ions

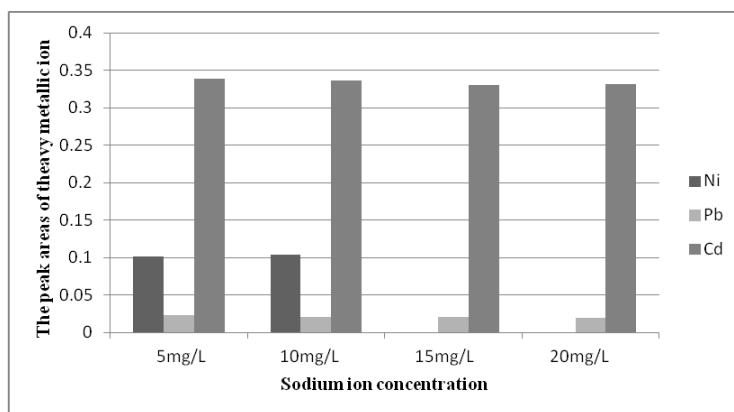


Figure 3. Influence of different Na⁺ concentrations on the peak area of heavy metallic ions.

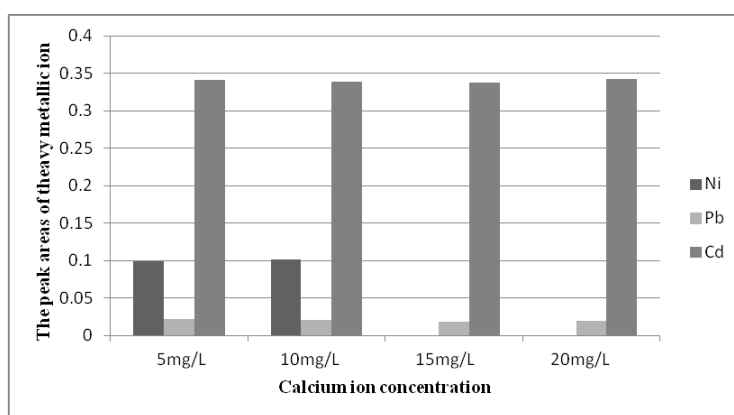


Figure 4. Influence of different Ca²⁺ concentrations on the peak area of heavy metallic ions.

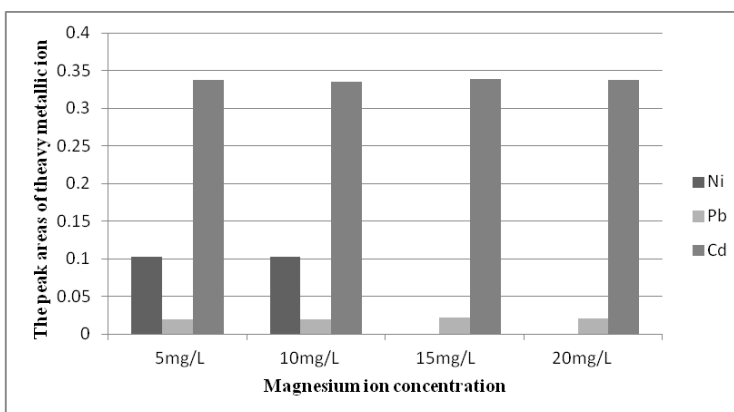


Figure 5. Influence of different Mg²⁺ concentrations on the peak area of heavy metallic ions.

3.3 Linear equation and detection limit

It is studied that the linear equation and detection limit of this determination method for three heavy metal ion by ion chromatography. The results show in Table 3. This method is simple, fast and has the advantage of good reproducibility.

Table 3. linear regression equations and detection limits of three metals elements.

No.	linear equations	R ²	Detection range (mg/L)	Detection limits (mg/L)
Ni	$y = 0.0041x + 0.0193$	0.9983	0.1-10	0.03
Pb	$y = 0.0012x + 0.0015$	0.9994	0.2-20	0.05
Cd	$y = 0.0142x + 0.0101$	0.9979	0.1-10	0.01

Next this method was used to detect the heavy metal in the surface soil of farmland in Xiang'an District. As was shown in Table 4. The soil of the tested area can reach the first grade standard.

Table 4. Contrast between the detection results and Environmental Quality Standard for Soils (mg/Kg).

Element	Sample	Recovery rate	Standard I	Standard II
Ni	23.18	94%	40	50
Pb	55.36	102.3%	90	300
Cd	Not detected	105%	0.2	0.3

4. Conclusions

In this study, a method has been developed for the determination of Ni, Pb and Cd in soils based ion chromatography with a high regression quality of squared correlation coefficient(0.9979-0.9994). The detected limits respectively are 0.03, 0.05 and 0.01. According to the experimental results, this method is rapid , high sensitivity and selectivity and low running cost.

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