Study on Determination of Seven Transition Metal Ions in Water and Food by Microcolumn High-Performance Liquid Chromatography

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A new method for the simultaneous determination of seven transition metal ions in water and food by microcolumn high-performance liquid chromatography has been developed. The lead, cadmium, mercury, nickel, cobalt, silver and tin ions were pre-column derivatized with tetra-(4-aminophenyl)-porphyrin (T_4-APP) to form the colored chelates which were then enriched by solid phase extraction with C_{18} cartridge. The enrichment factor of 50 was achieved by eluted the retained chelates from the cartridge with tetrahydrofuran (THF). The chelates were separated on a ZORBAX Stable Bound microcolumn (2.0×50 mm, 1.8 μm) with methanol-tetrahydrofuran (95 : 5, v/v, containing 0.05 mol/L pyrrolidine-acetic acid buffer salt, pH = 10.0) as mobile phase at a flow rate of 0.5 mL/min and detected with a photodiode array detector from 350-600 nm. The seven chelates were separated completely within 2.0 min. The detection limits of lead, cadmium, mercury, nickel, cobalt, silver and tin are 4 ng/L, 3 ng/L, 6 ng/L, 5 ng/L, 5 ng/L, 6 ng/L, 4 ng/L respectively in the original samples. This method was applied to the determination of the seven transition metal in water and food samples with good results.

Key Words : Microcolumn high-performance liquid chromatography, Tetra-(4-aminophenyl)-porphyrin, Transition metal ions

Introduction

The RP-HPLC technique with pre-column derivatization proved to be a favorable and reliable technique for the separation and determination of trace amounts of metal ions. Many kinds of reagents have been examined as pre-column derivatization regents, and several review articles on this approach have been published.[1-10] Among the various kinds of reagents, porphyrin ligands are useful because of the high molar absorptivity and high stability. The molar absorptivity of metal-porphyrin chelates above 10^5 is often found. Porphyrins can form very stable 1 : 1 chelates with many metal ions and these chelates are very stable during the HPLC separation.[1-5] Due to these facts, porphyrin reagents have, therefore, received increased attention and are frequently applied to the simultaneous determination of metal ions.[11-23]

However, the routine chromatographic methods need a long separation time (more then 10 min is needed). To shorten the separation time, in this paper, a ZORBAX Stable Bound microcolumn (2.0×50 mm, 1.8 μm) with pH range 1.5-12 was used for the separation of Hg-T_4-APP, Cd-T_4-APP, Pb-T_4-APP, Ni-T_4-APP, Co-T_4-APP, Ag-T_4-APP and Sn-T_4-APP chelates with pH 10 mobile phase. The seven chelates were separated completely within 2 min in this method. The separation time was greatly shortened compared to the routine chromatographic methods. Based on this, a rapid, sensitive and selective method for the simultaneous determination of seven transition metal ions in water and food was developed.

Experimental Section

Apparatus. The HPLC system consisted of a Waters 2690 Alliance separation model and a 996 photodiode array detector (Waters Corporation, USA). The pH values were determined with a Beckman Φ-200 pH meter. The absorbance measurement was performed with a Shimidzu UV-2401 spectrophotometer. The atomic absorption spectrometry analysis was carried out with a Shimidzu AA-6701F atomic absorption spectrophotometer.

The separation column used was a ZORBAX Stable Bound microcolumn (2.0×50 mm, 1.8 μm) (Agilent Corporation, USA). The cartridge used was Zorbax C_{18} solid phase extraction cartridge (1 cc/50 mg, 30 μm) (Agilent Corporation, USA). The extraction was conducted on Waters Solid Phase Extraction (SPE) Device (The device can prepare twenty samples simultaneously).

Chemicals. All solutions were prepared with ultra-pure water, which was obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Pb(II), Cd(II), Hg(II), Ni(II), Co(II), Ag(I) and Sn(IV) standard solution (1.0 mg/mL) were obtained from Chinese Standards Center, and a working solution of 0.2 μg/mL was prepared by diluting this standard solution. HPLC grade methanol and THF was obtained from Fisher Corporation, USA. Pyrrolidine-acetic acid buffer solution (0.5 mol/L, pH = 10) and TritonX-100 solution (2.0%(v/v)) were used in this experiment. T_4-APP was synthesized by our laboratory as described

in literature,[24] and was dissolved with THF to make a 1.5×10^{-4} mol/L of solution. All other reagents used were of analytical reagent-grade. The glass and Teflon wares used were soaked in 5% of nitric acid for a long time, and then thoroughly wash with pure water.

Two certified standard matreials, flour (GBW08426) and tea leaf (GBW08505) were obtained from Chinese Standards Center. The standard values of Pb, Cd, Hg, Ni, Co, Ag and Sn were determined by Atomic Absorption Spectrum (AAS), Atomic Fluorescence Spectrum (AFS), Neutron Activation Analysis (NAA), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-IES) and Ion Chromatography (IC) method.

Standard procedure. An appropriate volume of standard or the sample solution was transferred into a 50 mL of volumetric flask. To which, 5.0 mL of T_4-APP THF solution, 2 mL of Triton X-100 solution and 5 mL of 0.5 mol/L pH = 10 pyrrolidine-acetic acid buffer solution were added. The solution was diluted to volume of 50 mL with water and mixed well. The mixture was heated in boiling water bath for 15 min. After cooled, the solution was passed through the C_{18} cartridge at a flow rate of 10 mL/min. After the enrichment had finished, the retained chelates were eluted from the cartridge with 1.0 mL of THF at a flow rate of 5 mL/min in an opposite direction. The solution was filtered with 0.45 μm of filters and adjusted to the volume of 1.0 mL. 2.0 μL of sample was injected for HPLC analysis. A tridimensional (X axis: retention time, Y axis: wavelength, Z axis: absorbance) chromatogram was recorded from 350-600 nm with photodiode array detector and the chromatogram of 435 nm is shown in Figure 1.

Results and Discussion

The selection of porphyrin reagent. In this paper, seven porphyrin reagents, tetra-(4-bromophenyl)- porphyrin (T_4-BPP), tetra-(4-chlorophenyl)-porphyrin (T_4-CPP), tetra-(4-methoxyphenyl)-porphyrin (T_4-MOPP), tetra-(4-methyl-phenyl)-porphyrin (T_4-MPP), tetra-(4-sulfophenyl)-porphyrin (T_4-SPP), tetra-(4-hydroxyphenyl)-porpyrin (T_4-HPP) and tetra-(4-aminophenyl)-porpyrin (T_4-APP) were studied as pre-column derivatization regents for Co(II), Ni(II), Sn(IV), Hg(II), Pb(II), Ag(I) and Cd(II) ions. The experiment shows that all of the seven reagents can form colored chelates with Co(II), Ni(II), Sn(IV), Hg(II), Pb(II), Ag(I) and Cd(II). The T_4-MPP, T_4-CPP, T_4-MOPP, T_4-BPP and their metal-chelates show very poor solubility in water. It is required adding large proportion of organic solvents to improve the solubility, which is quite inconvenient. The T_4-SPP and T_4-HPP can form soluble chelates with metal ions. But in alkaline medium, their metal chelates have a poor retention on the reversed-phase column, because the sulfonic group or the hydroxy group on porphyrin reagents can ionize. The ion-pair reagent (quaternary ammonium salt) can greatly increase the retention of the metal chelates, whereas, the metal chelates gives peak tailing and can not separate completely in condition that the ion-pair reagent existed. The chromatograms in optimal condition were shown in Figure 2. So T_4-SPP and T_4-HPP are unsuitable as pre-column derivatization regents. T_4-APP can form soluble chelates in aqueous medium when Triton X-100 is existed. The chelates have good retention and peak shape on the reverse-phase column. Therefore, T_4-APP was selected as pre-column derivatization regent.

Precolumn derivation. According to the literature,[24-26] the optimal pH is 8.2-11.8 for the reaction of Co(II), Ni(II), Sn(IV), Hg(II), Pb(II), Ag(I) and Cd(II) with T_4-APP. Therefore, a 0.5 mol/L of pH = 10 pyrrolidine-acetic acid buffer solution was recommended to control pH. It was found that 1.0 mL of 1.5×10^{-4} mol/L T_4-APP THF solution was sufficient to complex 3.0 μg of Ni(II), Sn(IV), Co(II), Hg(II), Pb(II), Ag(I) and Cd(II). But in real samples, the foreign ions, such as Mg^{2+}, Pd^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Bi^{3+}, Ba^{2+}, Cu^{2+} and the like, can complex with T_4-APP to consume reagents.
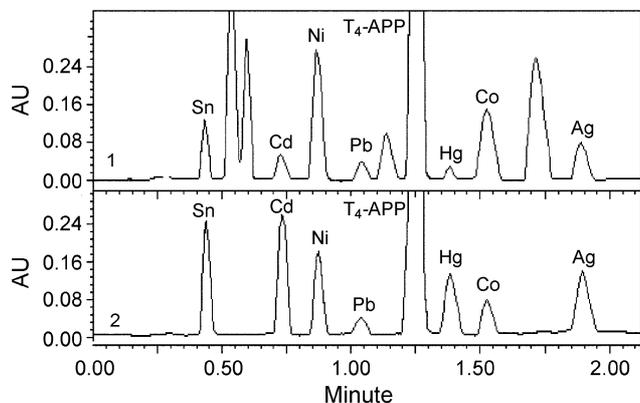

Figure 1. Chromatograms of standard sample and real sample: 1) Real sample (Flour sample), 2) Standard sample The Injection volume is 2.0 μL. Detection wavelength is 435 nm. Other conditions as in standard procedure.
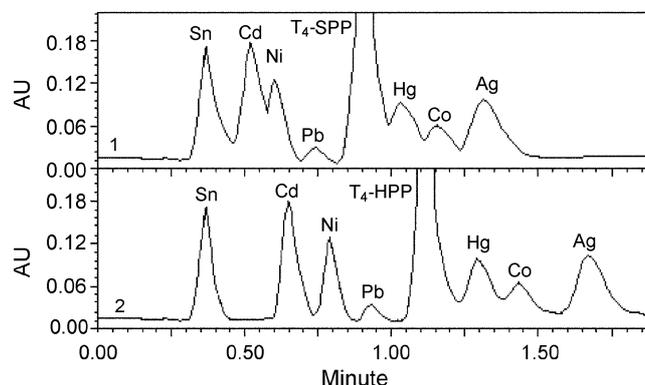

Figure 2. The chromatograms of metal T_4-SPP and T_4-HPP chelates in optimal condition. 1) metal-T_4SPP chelates (Mobile phase: acetonitrile/water (10 : 95), containing 0.05 mol/L pH 10.0 pyrrolidine-acetic acid buffer salt and 0.05 mol/L of tetrabutyl-ammonium nitrate). 2) metal-T_4HPP chelates (Mobile phase: acetonitrile/water (55 : 45), containing 0.05 mol/L pH 10.0 pyrrolidine-acetic acid buffer salt and 0.02 mol/L of tetrabutylammonium nitrate).

So more T_4-APP was needed. In this experiment, a 5.0 mL of 1.5×10^{-4} mol/L T_4-APP solution was recommended.

The reaction of Co(II), Ni(II), Sn(IV), Hg(II), Pb(II), Ag(I) and Cd(II) with T_4-APP was slow at room temperature. Heating accelerates the reaction. The reaction was complete after heating in boiling water bath for 10 min, and the chelate are stable for 5 h after cool, so heating for 15 min was selected.

Solid phase extraction. Both of the enrichment and the elution were carried out on a Waters SPE device (which can prepare twenty samples simultaneously). The flow rate was set to 10 mL/min for enrichment and 5 mL/min for elution.

Some experiments were carried out in order to investigate the retention of metal-T_4-APP chelates on the cartridge. It was found that the Sn-T_4-APP, Ni-T_4-APP, Co-T_4-APP, Hg-T_4-APP, Pb-T_4-APP, Ag-T_4-APP and Cd-T_4-APP chelates could be retained on the cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for metal-T_4-APP chelates was 32 mg in a 50 mL of solution. In this experiment, the cartridge has adequate capacity to enrich the metal-T_4-APP chelates.

In order to choose a proper eluant for the retained T_4-APP and its metal-chelates, various organic solvents were studied. It was found that the THF, isopentyl alcohol, acetonitrile, acetone, ethanol and methanol could elute the metal-T_4-APP chelates from cartridge quantitatively. For eluting the metal-T_4-APP chelates from cartridge, the volume of the solvent needed is THF 0.8 mL, isopentyl alcohol 1.3 mL, aceto-nitrile 1.6 mL, acetone 1.6 mL, ethanol 2.2 mL, methanol 2.4 mL. The maximal enrichment was achieved when THF was selected as eluant. The metal-T_4-APP chelates have a good stability in a weak alkaline medium. A 0.05 mol/L pyrrolidine-acetic acid buffer salt (pH=10) in THF can increase the stability of the metal-T_4-APP chelates during the elution, so it was selected as eluant. Experiment showed that it was easier to elute the retained T_4-APP and its metal-chelate on cartridge in reverse direction than in forward direction (Only 0.8 mL of eluant was needed when eluted in reverse direction. However, 2.2 mL of eluant was needed when eluted in forward direction), so it was necessary to upturned the cartridge during elution. 1.0 mL of THF (containing 0.05 mol/L pyrrolidine-acetic acid buffer salt (pH=10)) was sufficient for eluting the metal-T_4-APP chelate from cartridge quantitatively at a flow rate of 5 mL/min. An eluant volume of 1.0 mL was selected.

Spectrophotometric properties. The absorption spectrum of metal-T_4-APP chelates was obtained from tridimensional chromatogram recorded by photodiode array detector,. The maximum absorption wavelengths of Ni-T_4-APP, Sn-T_4-APP, Co-T_4-APP, Hg-T_4-APP, Pb-T_4-APP, Ag-T_4-APP and Cd-T_4-APP are 428 nm, 432 nm, 432 nm, 451 nm, 466 nm, 428 nm and 438 nm. To achieve maximum sensitivity, each metal-T_4-APP chelates were monitored at its maximum absorption wavelength.

Chromatographic separation. The Co-T_4-APP, Sn-T_4-APP, Ni-T_4-APP, Hg-T_4-APP, Pb-T_4-APP, Ag-T_4-APP and Cd-T_4-APP chelates were stable in weak alkaline medium. The pH of mobile phase within 8.5-11.8 can avoid the chelates decomposing and get a good peak shape. So methanol-tetrahydrofuran (95 : 5, v/v, containing 0.05 mol/L pyrrolidine-acetic acid buffer salt, pH=10.0) was selected as mobile phase. Because the routine silica based reverse phase bonded columns were not stable in pH 10, a ZORBAX Stable Bound microcolumn (2.0×50 mm, 1.8 μm) was selected as analytical column in this experiment. ZORBAX Stable Bound column have a good stability in pH 1.5-12.

Calibration. Under the optimum conditions, regression equations of metal-T_4-APP chelates were established based on the standard samples injected and their peak areas. Limits of detection are calculated by the ratio of signal to noise (S/N = 3). The results were given in Table 1. The reproducibility of this method was also examined for 10 mg/L of Ni(II), Sn(IV), Co(II), Pb(II), Cd(II), Ag(I) and Hg(II). The relative standard deviations (n=10) are also given in Table 1 too.

Interference. Under the pre-column derivatization condi-tion, the foreign ions of Mg^{2+}, Cu^{2+}, Pd^{2+}, Rh^{3+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Pt^{2+}, Ba^{2+}, Bi^{3+} and Ru^{3+} and the like react with T_4-APP to form color chelates. To examine the selectivity of this method, the interference of the routine foreign ions was investigated. When 5.0 mL of 1.5×10^{-4} mol/L T_4-APP was used, with 10 mg/L of Ni(II), Sn(IV), Pb(II), Co(II), Cd(II) and Hg(II) respectively, the tolerance amount with an error of $\pm$ 5% was 5000 μg/mL for Fe(III), Mg(II), 1000 μg/mL for Cu(II), Bi(III), Zn(II), Ba(II) and 500 μg/mL for Pd(II), Pt(II), Ru(III), Rh(III). The results show that most foreign ions do not interfere with the determination.

Applied to the food samples. 0.2-0.30 g of sample (wheat flour or green tea leaf) was weighed accurately into the

Table 1. Regression equation, coefficient and detect limit

Components	Regression Equation	Linear Range (μg/L)[a]	Coefficient	Detect limit (ng/L)[b]	RSD% (n=10)
Cd-T_4-APP	$A = 2.56 \times 10^6$ C+172	0.5 - 520	r = 0.9995	3	1.6
Pb-T_4-APP	$A = 2.12 \times 10^6$ C−125	0.6 - 620	r = 0.9996	4	2.2
Hg-T_4-APP	$A = 1.78 \times 10^6$ C+88.5	0.9 - 980	r = 0.9998	4	1.8
Ag-T_4-APP	$A = 1.26 \times 10^6$ C−76.4	0.9 - 980	r = 0.99958	6	2.1
Co-T_4-APP	$A = 2.16 \times 10^6$ C−138	0.6 - 830	r = 0.9997	5	1.8
Sn-T_4-APP	$A = 1.87 \times 10^6$ C+79.2	0.5 - 620	r = 0.9996	4	2.2
Ni-T_4-APP	$A = 2.04 \times 10^6$ C−128	0.6 - 620	r = 0.9998	5	1.7

[a]In the measured solution. [b]in the original digested sample.

Table 2. Determination results of certified standard food samples

Samples	Standard value (μg/g)	By this method (μg/g)	RSD % (n=5)
Flour (GBW08426)	As(0.285), Ag(−), Ba(21.2), Bi(0.342), Ca(2900), Cd(0.218), Ce(1.25), Co(4.71), Cr(3.76), Cu(10.2), Fe(54), Hg(0.086), Mg(360), Mn(6.3), Mo(0. 735), Ni(1.83), Pb(0.852), Sn(2.18)	Ag(−), Cd(0.202), Co(4.86), Hg(0.078), Ni(1.68), Pb(0.824), Sn(2.36)	2.2
Tea Leaf (GBW08505)	As(0.191), Ag(−), Ba(15.7), Ca(2840), Cd(0.128), Co(2.25), Cr(0.8), Cu(16.2), Fe(373), Hg(0.142), Mg(2240), Mn(766), Ni(5.61), Pb(1.06), Sn(1.24), Se(0.0412), Zn(38.7)	Ag(−), Cd(0.136), Co(2.11), Hg(0.136), Ni(5.84), Pb(1.18), Sn(1.38)	1.8

Table 3. Determination results (μg/L) of the water sample with this method

Components	Samples (μg/L)				RSD % (n=5)	Recovery % (n=5)
	River water	Lake water	Plant effluent	Tap water		
Co	18.5	14.6	56.8	12.8	1.8	98-101
Ni	26.2	15.8	44.2	16.2	2.3	97-103
Sn	16.7	31.5	28.5	8.67	3.1	96-104
Cd	5.46	11.2	16.7	2.22	2.2	97-104
Ag	8.61	18.7	18.6	−	1.8	95-101
Pb	12.5	8.65	22.8	6.58	2.1	96-102
Hg	2.87	5.62	12.5	−	1.7	98-105

Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). 2.5 mL of concentrated nitric acid and 2.5 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 5% of nitric acid and transferred into a 50 mL of calibrated flask quantitatively, then diluted the solution to volume with water. The Co, Ni, Sn, Hg, Pb, Ag and Cd contents were analyzed by using a proper volume of this solution according to general procedure. The results (deducted the reagents blank) were given in Table 2.

Applied to the water samples. For the fresh water (tap water, river water and lake water) the water sample was analyzed according to the general procedure. The results (deducted the reagents blank) were given in Table 3, together with the results of a recovery test by added 0.2 μg of Ni, Co, Sn, Ag, Pb, Cd and Hg in water sample and diluted to 50 mL

of final solution. For planting effluents, the sample was digested as literature[27] and analyzed according to the general procedure. The results (deducted the reagents blank) were given in Table 3 too, together with results of a recovery test by added 0.2 μg of Ni, Co, Sn, Ag, Pb, Cd and Hg in water sample and diluted to 50 mL of final solution. A standard method using atomic absorption spectrometry reported in literature[27] had also been used as a reference method. The results are also shown in Table 4.

Conclusion

In this paper, tetra-(4-aminophenyl)-porphyrin was firstly used as pre-column derivatization reagent for lead, cadmium, mercury, nickel, cobalt, silver and tin ions, and the ZORBAX Stable Bound microcolumn with pH range 1.5-12 was used for the separation of Hg-T$_4$-APP, Cd-T$_4$-APP, Pb-T$_4$-APP, Ni-T$_4$-APP, Co-T$_4$-APP, Ag-T$_4$-APP and Sn-T$_4$-APP chelates with pH 10 mobile phase. The seven chelates were separated completely within 2 min. Compared to the routine chromatographic method, more then 80% of separation time was

Table 4. Determination results (μg/L) of the water sample with reference method

Components	Samples (μg/L)				RSD % (n=5)	Recovery % (n=5)
	River water	Lake water	Plant effluent	Tap water		
Co	17.4	15.2	55.6	14.6	3.1	94-106
Ni	28.2	16.5	48.5	15.2	3.2	95-105
Sn	17.8	30.7	30.1	8.32	2.8	93-102
Cd	5.96	11.8	15.2	2.13	3.5	96-108
Ag	8.62	16.2	17.8	−	2.6	92-99
Pb	11.8	8.76	24.4	6.76	3.0	91-102
Hg	2.81	5.41	13.5	−	3.2	95-106

shortened. The metal-chelates were preconcentrated by C_{18} cartridge and the enrichment factor of 50 was achieved. The detection limits of this method reaches the ng/L level. Most foreign ions do not interfered with the determination. This is one of the sensitive, selective and rapid methods for the simultaneous determination of Ni, Co, Sn, Pb, Cd, Ag and Hg. In a word, for the simultaneous determination of Ni, Co, Sn, Pb, Cd, Ag and Hg in water and food, this method is high sensitivity, high selectivity and high rapidity.

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