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Determination of Lead, Iron, Manganese and Zinc in Sea Water Samples by Atomic Absorption Spectrometry after Preconcentration with Chromosorb 105

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Abstract

A solid phase extraction procedure based a column technique for preconcentration of lead, iron, manganese and zinc from water samples was developed. The analyte ions as its diethyldithiocarbamate complex were retained on a column of Chromosorb 105 from buffered sample solution. Then they were eluted with acetone. The recoveries of lead, iron, manganese and zinc under the optimum working conditions were 100, 97, 100 and 100%, respectively. The relative standard deviations were less than 6%. The method presented was applied for the determination of lead, iron, zinc and manganese in sea water samples.

Keywords: Preconcentration; Chromosorb 105; Lead; Iron; Manganese; Zinc; Solid Phase Extraction; Atomic Absorption Spectrometry

1. Introduction

Trace metal ions have important roles in our life functioning in a wide spectrum. Thus, the determination of trace metal ions is becoming increasingly important because of the increased interest in environmental samples including water, soil and plant, etc. Flame atomic absorption spectrometry is widely used due to its low cost, but its sensivity is usually insufficient for metal ions at ng L^{-1} concentration level. Also, the complex matrix interferences are another problem in the atomic absorption spectrometric determination of trace metal ions. Therefore, a preconcentration step that can not only concentrate the analytes but also simplify the matrix of the samples is usually desired strongly. Because of possessing the advantages of high preconcentration factor, low consumption of organic solvent and high recovery, solid phase extraction is one of widely used technique for the separation-preconcentration of trace elements carried out by using sorbents including activated carbon [1-6], sepiolite [7-14], ambersorb resins

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[15-20], amberlite XAD resins [21-32], diaion HP-20 [33–35], etc. Chromosorb-105 which is a methyl acrylate resin has a character of being resistant in concentrated mineral acid, concentrated bases and organic solvents for a long time. Its surface area, mesh size, and pore size are 650 g/m^2, 60–80 mesh and 40–60 nm, respectively. It is moderately polar. It was generally used in gas chromatography as stationary phase for the separation of some organic materials and for separation and preconcentration of some heavy metal ions in natural water samples [36–46].

In this work, the exploration about the potential of Chromosorb 105 as sorbent for preconcentration of Pb, Fe, Mn and Zn as diethyldithiocarbamate complexes from aqueous solution has been made. Several parameters influencing the recoveries of analytes, including pH of sample, sample volume, eluent volume and effect of divers ions have been investigated in detail. An optimized procedure has been applied to the determination of trace metals in water samples.

2. Experimental

2.1. Apparatus

Trace concentrations of metals were determined by FAAS using a Perkin Elmer Aanalyst 700 Model Atomic absorption spectrometer. The air-acetylene flame was adjusted according to the manufacturer's recommendations. A Hanna Instrument pH 211 microprocessor pH meter equipped with a combined glass calomel electrode was used for the pH adjustment. All solutions were delivered to pass through the glass column, having a stopcock and a porous disk was 10 cm long and 1.0 cm in diameter packed with Chromosorb 105.

2.2. Reagents and Solutions

All reagents were of analytical reagent grade unless stated otherwise and doubly distilled water was used through the experiments. Stock standard solution of 1000 mg L^{-1} metal ions was prepared by dissolving appropriate amount of nitrate salts in 1 % nitric acid. Chromosorb 105 was purchased from Phase Separation Inc., Norwalk, CT. The buffers used were phosphoric acid/dihydrogen-phosphate for pH 2, sodium acetate/acetic acid for pH 4 to 6 and ammonium hydroxide/ammonium chloride for pH 8 to 10.

2.3. Method Development

The column was dry-packed with 500 mg Chromosorb 105. A small amount of glass wool was placed on the disc to prevent the loss of the resin during sample loading. The bed height of resin bed was approximately 1.5 cm. It was washed successively with water, acetone and water, respectively. The column was preconditioned by passing blank solution prior to use. After each use, the resin in the column was washed with large volumes of water and stored in water for the next experiment.

The performance of column method was tested with model solution before its application to the samples. 100 mL of the model solution containing 20 µg Pb, 10 µg Fe, 10 µg Mn and 5µg Zn was buffered to desired pH. 3 mL of 0.05 % m/v NaDDTC solution was added to this solution. It was loaded to the top of the preconditioned column and gravitationally passed through at a flow rate of 2 mL min^{-1}. The column was washed with 5-10 mL of blank solution prepared with the corresponding buffer solution. Then, the retained metal ions were eluted with 10 mL of acetone. Acetone was evaporated to near dryness on a hot plate adjusted to ca. 30-40 ^{o}C and then cooled. The analytes in the effluent were determined by FAAS.

2.4. Analysis of Water Samples

The surface sea water samples were collected in pre-washed polyethylene bottles from a dirty region of Aliağa Bay. The bottles were cleaned with detergent, double distilled–deionized water, a dilute nitric acid and double distilled–deionized water, respectively. The samples were immediately filtered through a Millipore cellulose nitrate membrane having pore size 45 µm, acidified to pH 3 with hydrochloric acid and stored in precleaned polyethylene bottles. The samples were analyzed with the preconcentration procedure given above, within a week after their collections. For the analysis, the acidified sea water was firstly neutralized and then buffered to desired pH. The preconcentration procedure given above was submitted to these solutions.

3. Results and discussion

3.1. Effects of pH

The effect of the pH on the retention of Pb, Fe, Mn and Zn as diethyldithiocarbamate complexes on the Chromosorb-105 resin column was studied by applying of the proposed procedure at different pH values (Fig.1). The results indicate that the recoveries for Pb and Fe were found as 96% at pH 6, 97% at pH 4, respectively. The recoveries of both of Mn and Zn were found 100% at pH 9. Due to these results, the further studies were performed at pH 6 for Pb, at pH 4 for Fe and at pH 9 for both of Mn and Zn.

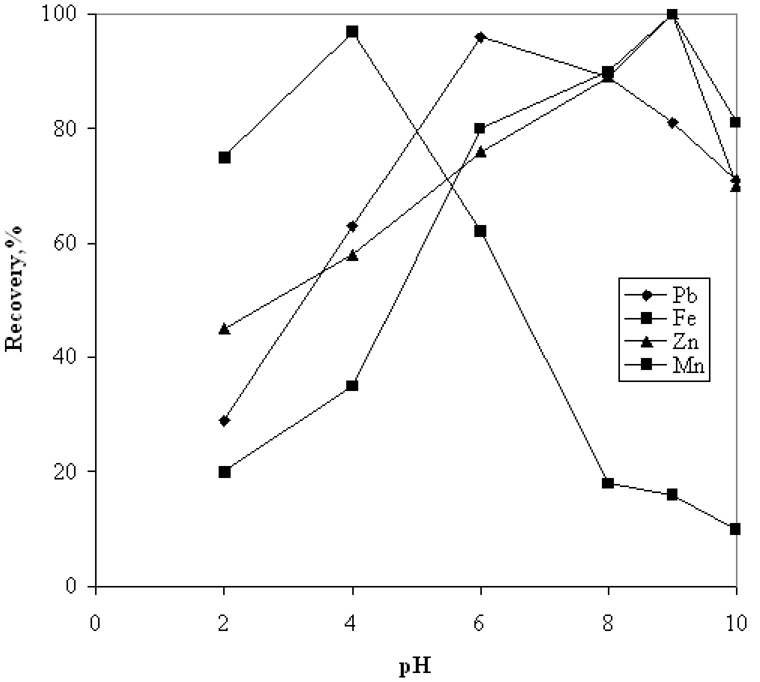

Fig.1. The effect of pH on the recovery of metal-DDTC complexes

3.2. Influences of Eluent Type

To investigate the effect of elution solution, various eluents such as HNO_3 at the concentration range of 0.5, 1.0 and 1.5 mol L^{-1} and HCl at 0.5, 1.0 and 1.5 mol L^{-1}, acetone and 0.01 mol L^{-1} EDTA were tested. The results are shown in Table 1. As can be seen, the maximum recovery values were obtained with EDTA solution for Pb, pure acetone for Fe, Mn and Zn. Also the quantitative recovery for Pb was obtained with pure acetone. As being practical pure acetone was used for all elements as the eluent throughout the experiments. The volume of eluent was 10 mL.

Table 1: Influences of the various eluents on the desorption of metal-DDTC complexes

Eluent type	Concentration, mol L^{-1}	Recovery*, %			
		Pb	Fe	Mn	Zn
HCl	0.5	16	28	55	46
	1.0	33	52	66	61
	1.5	83	59	62	68
HNO_3	0.5	16	23	31	52
	1.0	49	21	38	67
	1.5	50	29	43	71
EDTA	0.01	100	33	23	35
HCl/HNO_3 (1:3, v/v)	1.0	62	42	41	64
HCl/HNO_3 (3:1, v/v)	1.0	87	23	53	55
Acetone	-	96	97	100	100

*The mean of three replicates

3.3. Effect of Sample Volume

The effect of sample volume on the retention of metal ions was studied by varying the sample from 25 to 1500 mL. As can be seen in Fig.2, the recoveries of Pb and Fe were quantitative until 1250 and 50 mL, respectively. But, the recoveries of Mn and Zn were quantitative until 250 mL. Although a high preconcentration factor (125) was obtained for Pb, it was 5 for Fe, and 25 for both Mn and Zn. From these results, the method could be applicable for the determination of Pb, Fe, Mn and Zn in environmental samples, such as sea water.

3.4. Precision of the method

The precision of the determination of lead, iron, manganese and zinc was evaluated under the optimum conditions mentioned above. For this purpose, five successive retention and elution cycles (with 20 µg Pb, 10 µg Fe, 10 µg Mn and 5µg Zn in 100 mL of solution) were performed. It was found that the recovery of lead, iron, manganese and zinc were 100±4, 97±6, 100±3 and

100±4 at 95% confidence level, respectively. In conclusion, the precision of the method is very good, and the recovery of the analyte is quantitative (>95%).

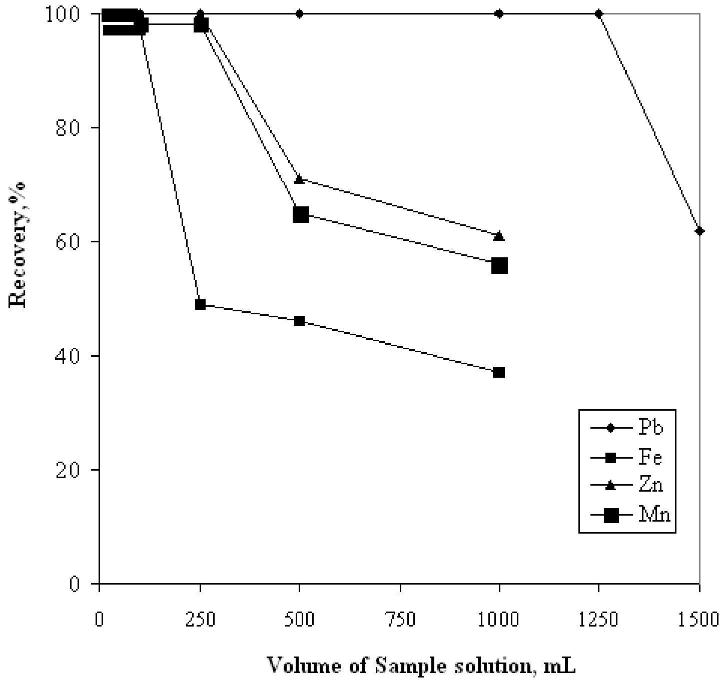

Fig.2. The effect of volume of solution on the recovery of metal-DDTC complexes

Table 3. Precision of the method

Element	Recovery[a],% R ± ts/√N	Relative standard deviation, s/x	N
Pb	100 ± 4	0.038	6
Fe	97 ± 6	0.057	6
Mn	100 ± 3	0.032	6
Zn	100 ± 4	0.037	6

[a] Average of N determinations with 95% confidence level

3.5. Matrix Effects

The influence of interferences will come mainly from the major matrix ions in the water samples such as Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} on the preconcentration of Pb, Fe, Mn and Zn ions on Chromosorb 105 were investigated. To investigate the effect of matrix ions, 100 mL of solution containing 20 µg of each metal ions and coexisting the ion with varying concentrations was prepared. The recommended preconcentration and analytical procedure was applied to these solutions. It was found that the major matrix ions in the natural water samples show no obvious interference on the preconcentration with developed method of some trace metal ions (Table 3). The tolerable concentration for Na^+ was 10000, mg L^{-1} and that for K^+, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} was 1000 mg L^{-1}.

Table 3. The influence of the foreign ions on the recovery of metal

Ion	Concentration µg mL^{-1}	Recovery*, %			
		Zn	Pb	Fe	Mn
Na^+	500	95	98	96	96
	1000	100	100	97	98
	2500	98	100	98	99
	5000	99	96	100	100
	10000	98	97	98	100
K^+	500	100	102	94	99
	1000	99	91	98	99
	2500	95	55	97	97
Mg^{2+}	500	99	97	98	100
	1000	97	96	100	100
	1500	98	96	98	96
Ca^{2+}	500	100	98	94	98
	1000	100	85	88	99
	2500	97	55	90	97
SO_4^{2-}	500	97	96	95	98
	1000	97	98	97	96
	2500	100	93	98	99
HCO_3^-	500	96	95	96	95
	1000	98	85	79	95
	2500	96	70	82	100

*The mean of three replicates

3.6. Capacity studies

The capacity study used was adapted from that recommended by Maquieira et al. [47]. The procedure has been given in Ref [8].

As shown in Table 4, the breakthrough capacities were found as 4.2, 8.0, 52.3 and 67.7 µmol g^{-1} for lead, iron, manganese and zinc, respectively.

Table 4. Adsorption capacity

Element	Adsorption capacity*	
	(mg g^{-1})	(μmol g^{-1})
Pb	0.861	4.2
Fe	0.447	8.0
Mn	0.287	52.3
Zn	0.443	67.7

*The mean of three replicates

3.6. Accuracy and Application

The developed method was applied to analysis of seawater samples. To estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked to 500 mL of seawater samples. The resulting solutions were submitted to preconcentration procedure. Iron and zinc were determined by FAAS, on the other hand, lead and manganese were determined by GF-AAS. The recoveries of spiked analytes are given in Table 4. A good agreement was obtained between the added and measured analyte amounts in sea water. These results confirm the validity of the proposed method.

Table 4. Determination of lead, iron, magnesium and zinc in sea water

	Added, μg/L	Found, μg/L	Recovery[a],%	% s/x
Pb	-	0.052 ± 0.002	-	-
	0.050	0.104 ± 0.004	104.0	3.8
	0.100	0.154 ± 0.005	102.0	3.2
Fe	-	40.8 ± 0.3	-	-
	50	87.2 ± 6.4	98.0	7.3
	100	129.4 ± 2.2	98.8	1.7
Mn	-	0.303 ± 0.06	-	-
	0.300	0.601 ± 0.02	99.3	5.2
	0.600	0.897 ± 0.07	98.0	7.8
Zn	-	187 ± 0.03	-	-
	100	279 ± 5.4	95.7	1.9
	200	382 ± 3.6	97.3	0.9

*The mean of three replicates

4. Conclusion

The proposed method for the determination of metal-DDC complexes provides a simple, easier and accurate for the preconcentration and separation of trace amounts. The method has been successfully applied to environmental samples.

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References

1. Vanderborght B M and Van Grieken R E (1977) Enrichment of trace metals in water by adsorption on activated carbon. Anal Chem 49 (2): 311.
2. Takara E A, Pasini-Cabello S D, Cerutti S, Gasquez J A and Martinez L D (2005) On-line preconcentration/determination of copper in parenteral solutions using activated carbon by inductively coupled plasma optical emission spectrometry. J Pharm Biomed Anal 39: 735.
3. Murty D S R and Chakrapani G (1996) Preconcentration of rare earth elements on activated carbon and its application to groundwater and sea-water analysis. J Anal At Spectrum 11: 613.
4. Lee S H and Choi H S (2003) Determination of copper after preconcentration as its 1-nitroso-2-naphthol complex onto activated carbon. Bull Korean Chem Soc 24 (11): 1705
5. Soylak M and Doğan M (1996) Column preconcentration of trace amounts of copper on activated carbon from natural water samples. Anal Lett 29: 635.
6. Soylak M, Narin İ and Doğan M (1997) Trace enrichment and atomic absorption spectrometric determination of lead, copper, cadmium and nickel in drinking water samples by use of an activated carbon column. Anal Lett 30: 2801.
7. Türker A R, Bağ H, Erdoğan B (1997) Determination of iron and lead by flame atomic absorption spectrometry after preconcentration with sepiolite. Fresenius J Anal Chem 357 (3): 351.
8. Bağ H, Lale M and Türker A R (1998) Determination of iron and nickel by flame atomic absorption spectrophotometry after preconcentration on Saccharomyces cerevisiae immobilized sepiolite. Talanta 47 (3): 689.

9. Bağ H, Lale M and Türker A R (1999) Determination of Cu, Zn and Cd in water by FAAS after preconcentration by baker's yeast (Saccharomyces cerevisiae) immobilized on sepiolite. Fresenius J Anal Chem 363 (3): 224.
10. Bağ H, Türker AR, Lale M (1999) Determination of trace metals in geological samples by atomic absorption spectrophotometry after preconcentration by Aspergillus niger immobilized on sepiolite. Anal Sci 15 (12): 1251.
11. Bağ H, Türker A R and Lale M (2000) Determination of Cu, Zn, Fe, Ni and Cd by flame atomic absorption spectrophotometry after preconcentration by Escherichia coli immobilized on sepiolite. Talanta 51 (5): 1035.
12. Tunçeli A, Bağ H and Türker A R (2001) Spectrophotometric determination of some pesticides in water samples after preconcentration with Saccharomyces cerevisiae immobilized on sepiolite. Fresenius J Anal Chem 371(8):1134.
13. Bağ H, Türker AR, Tunçeli A, Lale M (2001) Determination of Fe(II) and Fe(III) in water by flame atomic absorption spectrophotometry after their separation with Aspergillus niger immobilized on sepiolite. Anal Sci 17 (7): 901.
14. Doğan C E and Ünel K (2002) Sorption and preconcentration of some trace metals on sepiolite. Ann Chim 92: 1171.
15. Narin, I.; Soylak, M.; Kayakirilmaz, K.; Elci, L.; Dogan, M. Speciation of Cr(III) and Cr(VI) in tannery wastewater and sediment samples on ambersorb 563 resin. Anal. Lett. 2002, 35, 1437–1452.
16. Saraçoğlu S, Soylak M and Elci L (2003) The Enrichment/Separation of Fe, Co, Pb, Cd, and Cr on Ambersorb 563 Prior to Their Flame Atomic Absorption Spectrometric Determinations. J Anal Chem 58 (12): 1127.
17. Narin İ and Soylak M (2003) The Uses of 1-(2-Pyridylazo) 2-Naphtol (PAN) Impregnated Ambersorb 563 Resin on the Solid Phase Extraction of Traces Heavy Metal Ions and their Determinations by Atomic Absorption Spectrometry. Talanta 60: 215.
18. Saraçoğlu S, Soylak M and Elçi L (2003) Determination of Trace Amounts of Copper in Natural Water Samples by Flame Atomic Absorption Spectrometry Coupled to Flow Injection On-Line Solid Phase Extraction on Ambersorb 563 Adsorption Resin. Chemia Analityczna (Warsaw) 48: 77.
19. Baytak S and Türker A R (2006) Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA. J Hazard Mater B129: 130.

20. Kendüzler E and Türker A R (2002) Determination of Iron, Manganese and Zinc in Water Samples by Flame Atomic Absorption Spectrophotometry after Preconcentration with Solid-Phase Extraction onto Ambersorb 572. Anal Sci 18(8): 917.
21. Türker A R and Tunçeli A (1993) Preconcentration of copper, nickel and zinc with Amberlite XAD-16 resin, Fresenius J. Anal. Chem 345: 755
22. Tunçeli A and Türker A R (1999) Determination of gold in geological samples and anode slimes by atomic absorption spectrometry after preconcentration with Amberlite XAD-16 resin. Analyst 122 (3): 239.
23. Tewari P K and Singh A K (2000) Amberlite XAD-7 impregnated with Xylenol Orange: a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS. Fresenius J Anal Chem 367(6):562.
24. Tunçeli A and Türker AR (2000) Determination of palladium in alloy by flame atomic absorption spectrometry after preconcentration of its iodide complex on Amberlite XAD-16 Anal Sci 16 (1): 81.
25. Tunceli A and Türker AR (2000) Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution Talanta 51 (5): 889.
26. Soylak M, Elci L and Dogan M (2001) Solid phase extraction of trace metal ions with amberlite XAD resins prior to atomic absorption spectrometric analysis. J Trace Microprobe Techn 19: 329.
27. Wuilloud R G, Wuilloud G M, Wuilloud J C A, Olsina R A, Martinez L D (2002) Preconcentration and speciation of Cr(III) and Cr(VI) in water samples using amberlite XAD-16 resin and determination by flow injection flame AAS. Atom Spect 23(2): 44.
28. Doğutan M, Filik H, Demirci S, Apak R (2002) The Use of Palmitoyl Hydroxyquinoline-Functionalized Amberlite XAD-2 Copolymer Resin for the Preconcentration and Speciation Analysis of Gallium(III). Sep Sci Tech 35 (13): 2083.
29. Türker A R and Baytak S (2004) The Use of Escherichia coli Immobilized on Amberlite XAD-4 as Solid Phase Extractor for Metal Preconcentration and Determination by Atomic Absorption Spectrometry. Anal Sci 20: 329.
30. Baytak S and Türker A R (2004) Flame Atomic Absorption Spectrometric Determination of Manganese in Alloys after Preconcentration onto Amberlite XAD-4 Loaded with Saccharomyces carlsbergensis. Turk J Chem 28: 243.

31. Baytak S and Türker A R (2005) The use of Agrobacterium tumefaciens immobilezed on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron(III), cobalt(II), manganese(II) and chromium(III). Talanta 65(4): 938.
32. Baytak S and Türker A R (2005) Determination of Iron (III), Cobalt (II) and Chromium (III) in Various Water Samples by Flame Atomic Absorption Spectrometry After Preconcentration by Saccharomyces carlsbergensis Immobilized on Amberlite XAD-4. Microchim Acta 149 (1-2) 109.
33. Soylak M, Armağan F, Elçi L and Doğan M (2001) A new preconcentration and separation method for flame atomic absorption spectrometric determinations of some trace metal ions on a diaion HP-20 column. Ann Chim 91,(9-10): 637.
34. Soylak M (2002) Nickel Determination in samples with high salt content by atomic absorption spectrometry after enrichment/separation on Diaion HP-20. Quim Anal 20: 175.
35. Soylak M, Akkaya Y and Elci L (2003) Application of the solid phase extraction procedure on chromatographic mini column filled with Diaion HP-20 for determination of copper, cobalt, cadmium, iron and manganese in textile products and textile wastewaters. Trace Elem Electroly 20: 16.
36. Armağan F, Soylak M, Elçi L, Doğan M (2002)Solid phase extraction of some metal ions on Diaion-20 resin prior to flame atomic absorption spectrometric analysis. J Trace and Microprobe Techn 20:15.
37. Elci L, Arslan Z and Tyson J F (2000) Flow injection solid phase extraction with chromosorb 102: determination of lead in soil and waters by flame atomic absorption spectrometry. Spectrochim Acta 55B: 1109.
38. Cai Y, Jiang G and Liu J (2001) Preconcentration of trace amounts of cadmium in aqueous samples on mini columns packed with chromosorb series gas chromatographic stationary phases and its determination by electrothermal atomic absorption spectrometry. Analyst 126: 1678.
39. Cai Y, Jiang G.B, Liu J F and Liang X (2002) Solid phase extraction of trace amounts of lead derivatized with 8-hydroxyquinoline using a GC stationary phase mini -column packed with chromosorb 105. Atom Spectr 23: 52.
40. Saraçoğlu S, Soylak M, Elçi L and Doğan M (2002) Determination of Cu, Fe, Ni, Co, Pb, Cd, Mn and Cr in natural water samples after solid phase extraction on Chromosorb 102. Anal Lett 35: 2603.

41. Saraçoğlu S, Soylak M, Dogan M and Elci L (2003) Speciation of antimony using Chromosorb 102 resin as a retention medium. Anal Sci 19: 259.
42. Tuzen M and Soylak M (2006) Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108. J Hazard Mater B129: 266.
43. Karatepe A U, Soylak M and Elci L (2003) Separation/preconcentration of copper, lead, and iron in natural water samples on Chromosorb-105 resin prior to flame atomic absorption spectrometric determinations. Atom Spectr 36 (4): 797.
44. Saraçoğlu S and Elci L (2002) Column solid-phase extraction with Chromosorb-102 resin and determination of trace elements in water and sediment samples by flame atomic absorption spectrometry. Anal Chim Acta 452: 77.
45. Cai Y, Jiang G and Liu J (2002) Preconcentration of cobalt with 8-hydroxyquinolinea nd gas chromatographic stationary phase Chromosorb 105 and its determination by graphite furnace atomic absorption spectrometry. Talanta 57: 1173.
46. Yao J, Liu Y, Tuo Y, Zhou F, Zhang J, Xiao Y, Xiao S and Tan Z (2004) Solid-Phase Extraction of Nickel from Electrolytic Manganese using a “Sorbent in Syringe” Technique for Electrothermal Atomic Absorption Spectrometry. Can J Anal Sci Spectrosc 49: 267.
47. Maquieira A, Elmahadi H A M, and Puchades R (1994) Immobilized cyaaobacteria for on-line trace metal enrichment by flow injection atomic absorption spectrometry. Anal Chem 66: 3632.

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