

The method for Determination of heavy Metals in Natural Water by Solid phase Collection

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Abstract :

In this study used graphite furnace atomic absorption for determination of the trace heavy metals (As, Cr, Pb, and Cd) in natural water samples after collection and concentration by chelating resin disk . A miniature filtering apparatus was improved to be able to use 6 mm diameter chelating resin disk . Collection of heavy metals in 25 ml of sample solution was finished within 10-25 min by suction and elution was accomplished within 15 min by ultra sanitation . For the elution relatively dilute acid concentration 0.2 M HNO_3 . Several metals, As , Cr, Pb and Cd could be determined.

Introduction :

It would seem that natural water should be comparatively easy to analyze, from the point of view of preconcentrating and determining its components, including the heavy metals. Several methods can be applied to separate the trace quantities of these metals from the matrix evaporation of water, recovery of trace components by solvent extraction or sorption methods. However, heavy metals can exist in various states in natural water, and it is, therefore, necessary to take measures aimed at obtaining the forms suitable for a positive analytical effect to be reached. ⁽¹⁻²⁾

In river water the concentration of the heavy metals is often trace levels lower than limit of detection (LOD) of highly sensitive instruments such as GF- atomic absorption , ICP – MS and ICP- AES ⁽³⁾ .

The determination of trace metals become increasingly Important in such fields as advanced materials , earth science , environment and biology

The treatment of partial samples , Separation from coexisting substances and concentration to the measurable concentration level is necessary , ⁽⁵⁾ such as co precipitation , solvent extraction and chelating resin adsorption, ⁽⁶⁾ but these separations concentration method for elements have some disadvantages handling of harmful organic solvent,

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relatively large sample volume, complicated procedure, reduce of concentration efficiency by elution and contamination from chemicals used⁽⁶⁻⁸⁾. In general a batch wise method⁽⁹⁾ with chelating resins such as Chelex – 100 is popular, but it needs much sample volume, relatively high concentration of nitric acid as eluent, and much waste. Column treatment method with chelating resin was also adopted in many papers which has some disadvantages, it is time consuming for passing solutions through the resin column, such as column conditioning sample, washing and elution solutions some papers⁽⁹⁾ were reported the determination of several heavy metals in water samples by graphite atomic absorption after the preconcentration using a chelating resin disk. The collection efficiency and recovery were good. Their experimental conditions, however, were a somewhat large scale system. For examples required sample volume were 30 ml for enough concentration.

T. Osaki et al.⁽¹⁰⁾ reported metal ions were collected on a miniature membrane filter as an ammonium pyrrolidine dithiocarbamate chelates. Collection / concentration was carried out by membrane filtration and dissolution the membrane into small volume of organic solvent. Concentration efficiency was accomplished by minimizing the apparatus which was able to use 0.4 cm diameter membrane, resulting diminishing the sample volume, reagent consumption and waste. But effective collection on a membrane filter required the addition of polyvinyl alcohol as dispersion and adsorption the precipitate which caused somewhat complicated procedure. In this paper, simple and effective method was developed for the determination of ultra trace amount of heavy metals by collection and concentration the metals by a chelating resin and filtering apparatus.⁽¹¹⁻¹²⁾ Chelating resin disk had thickness compared with membrane filter, chelating resin disk can be absorbed many metal ions. As, Cr, Pd, and Cd were determined by atomic absorption. The proposed method was applied to the river water samples in Mahaweel.

Experimental :

Reagents

The purest metal salts of nitrate (As, Cr, Pb and Cd) (fisher) were used to prepare 100 µg / ml stock solutions. Ammonium formate buffer, pH (9.6) was prepared by dissolving 15 (g) tartaric acid in 250 ml of 0.2M ammonium solution. Stock solution of 0.1M nitric acid was prepared. An iminodiacetic chelating resin disk used to punch in a diameter of 4 mm.

All diluted solutions were prepared by dilution of stock solutions.

Apparatus

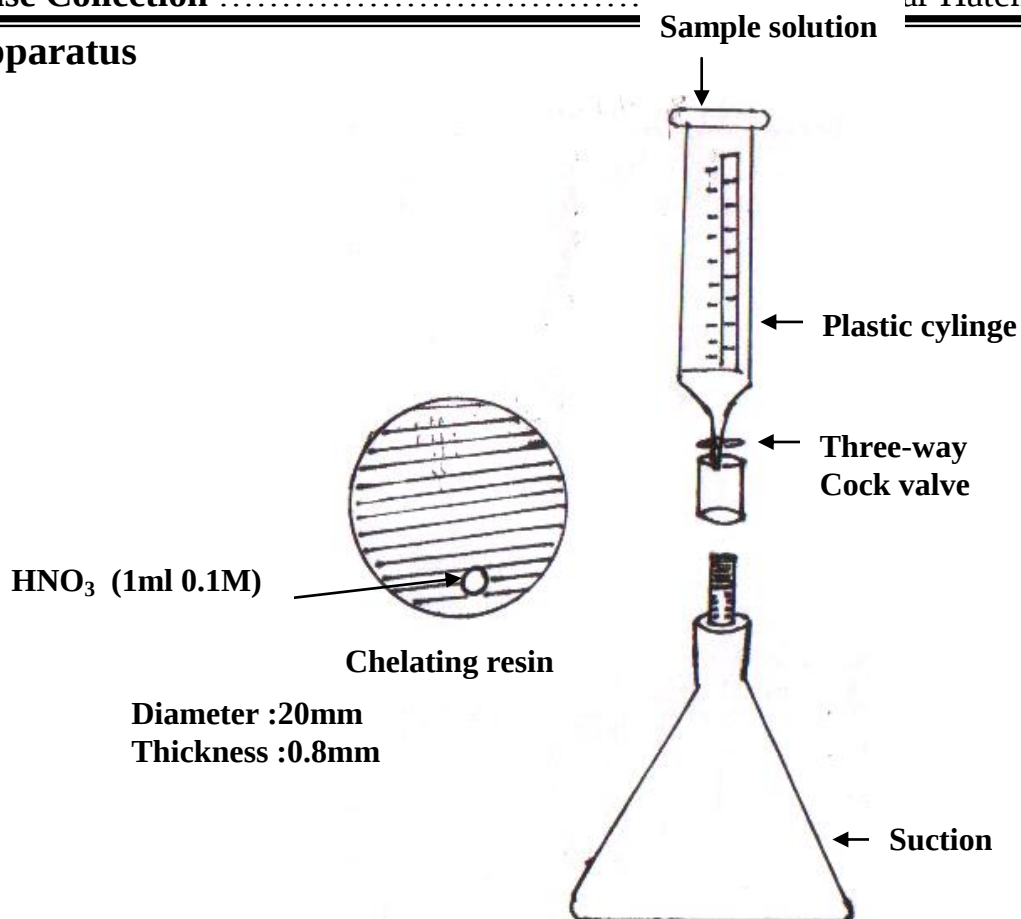


Fig (1) : Show the chelating resin and solid phase collection

Analysis of the sample extracts was done by grafite atomic absorption spectroscopy (GAAS). A mini scale filtering apparatus was improved for using a chelating resin disk which had thickness Ultrasonication bath was used to elute heavy metals from absorbed chelating resin desk transferred in a tiny capped vial .

The method

6 mm diameter disk of chelating resin cut and put on the filtering support , it was conditioned to pH (5-6) with acetic acid and ammonium acetate buffer solution. Sample solution (25 ml) adjusted to pH (5-6) by adding one drope of buffer and some drops of ammonium hydroxide.

Then it was passed through the disk by suction for 15 min. The chelating resin disk was washed with 5 ml of pure water, then put: into a vial (2ml volume with cup) and 0.25 -1 ml of 0.1 M nitric acid was added , followed ultrasonication for 20 min. The eluate was set to the autosampler and measured by GAAS.

Result and Discussion :

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Grafit atomic absorption spectrometer measurement conditions for As , Cr , Pb, and Cd were shown in table (1) . Effect of pH on absorption of metals was examined from (pH = 2 to pH =11) for each element. In this study, for simple procedure chelating resin disk was selected for collection and concentration instead of chelating resin column and the filtering precipitate with membrane filter was improved for the disk, to achieve high sensitivity with less sample volume and chemicals.

Table (1) : The condition of GAAS for the determination of As , Cr , Pb , and Cd .

No.	Condition (a)	As	Cr	Pb	Cd
1.	Lamp current	9.8 mA	10.5 mA	11 mA	11.2 mA
2.	Flow rate	200ml / min	280ml/min	250ml/min	269ml/min
3.	Wave length	325nm	422nm	312 nm	229 nm
4.	Slit width	0.82 nm	0.75nm	0.78 nm	0.8 nm
5.	Sample volume	30 µl	30 µl	30 µl	30 µl
6.	Drying temperature	150 °C	140 °C	110 °C	125 °C
7.	Ashing temperature	(720-750°C)	(700-720°C)	(620-650°C)	(680-700°C)
8.	Atomization temperature	(1600-1620°C)	(1700-1730°C)	(1500-1550°C)	(1580-1620°C)
9.	Cooling temperature	25°C	25°C	25°C	25°C
10.	Cleaning temperature	2650°C	2750°C	2550°C	2700°C

a : Average of four determination

Concentration efficiency was tested with µg / ml chromium III standard solution . A chelating resin disk in 4 mm diameter can be immersed in minimum 0.25 ml of eluting solvent . GAAS used is sufficient to measure one sample solution only 30 µl , if eluent is 0.25 ml , It is possible for 5 measurements. By varying sample volumes from 10 to 50 ml and eluent volumes from 0.25 to one ml, concentration efficiency was examined and the result were shown in table (2) .

Table (2) : Concentration Efficiency for Chromium III .

No.	Conc. (ppm)	RSD%	Added Conc. (ppm)	Recovery	Peak area n=3
1.	50-fold	1.72	5	99	0.029, 0.031, 0.033
2.	75-fold	1.80	7.5	98	0.044, 0.045, 0.016
3.	100-fold	2.10	10	99	0.058, 0.060, 0.062
4.	150-fold	3.20	15	97.8	0.087, 0.089, 0.091
5.	200-fold	5.2	20	97	0.118, 0.120, 0.122

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Concentration ratio to 200 fold can be attained by simple procedure when larger syringe than 50ml volume can be available, more concentration can be achieved, because chelating resin disk have enough absorbing ability.

We examined optimum suction and ultrasonication time with 0.25 µg/ml cadmium standard solution.

Suction time for sample solution filtering through the disk was proportional to the volume of sample solution. The results obtained by changing ultrasonication time from (5) to (50) min. were shown in figure (2). The recovery of cadmium II was 98% above 15 min. and stable for two hours.

Total processing time for the pretreatment was about 30 min. which was shorter 0.2 than that of resin column treatment.

Table (3): Analytical results of Cr(III), Cd(II), Pb(II) and Hg in Mahaweel river waters by GF. AAs.

Metal ions	Detection limit PPb	RSD%	Metal conc. µg/ml
Cr	12.1	3.6	0.05
Cd	32.0	2.6	0.01
Pb	47.0	1.2	0.12
As	9.2	2.4	0.06

Table (4): Cd(II) recovery for 0.25 µg/ml Cd⁺² conc. With sample volume 15ml.

Time(min.)	5	7	10	13	15	20	25	30	40	50	60
Rec%	26	35	50	67	78	80	80	80.02	80.0	80.02	80.0

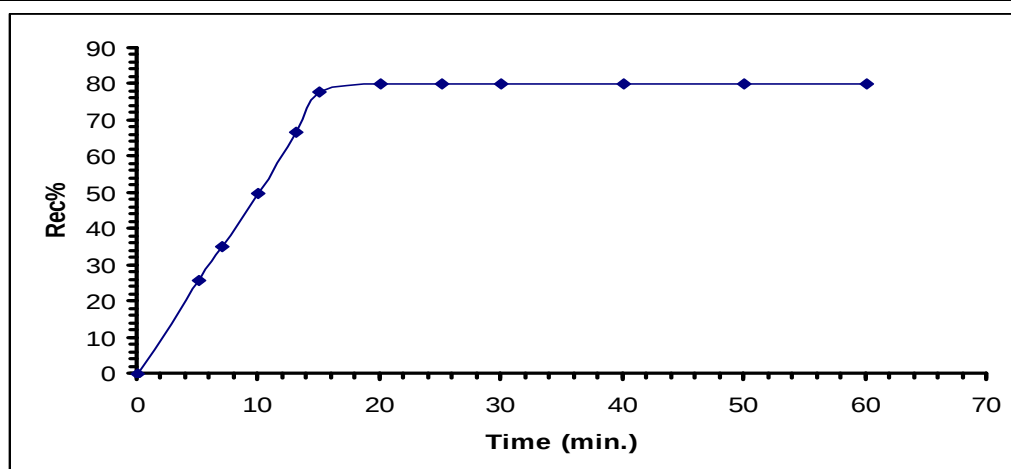


Figure (3): Ultrasonic time effect on Cd(II) recovery Cd^{+2} Conc. 0.25 $\mu g/ml$, eluent volume 2ml and sample volume (15ml).

Reproducibility test was carried out with 0.25 $\mu g/ml$ Cd^{+2} standard solution. Table (3) described the relative standard deviation and the detection limit for the elements (As, Cr, Cd, Pb). The effect of matrix ions was tested. Matrix ions were examined by GFAAs.

Mahaweel river water contained each heavy metal (As, Cr, Pb, Cd) by different concentration in 0.1 M nitric acid.

The sample solution (12 ml^{-1}) was analyzed by the procedure. The result of the recoveries were almost 99% for As matrix and 98% for Pb and Hg matrix but 97% for Cd matrix. This method could be applied to each river or sea water analysis.

This study has some advantages such as high concentration efficiency of a small measuring volume, simple and short time.

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الخلاصة:

تم في هذه الدراسة استخدام تقنية الامتصاص الذري غير اللهبى باستخدام فرن كرافيتي لتقدير بعض العناصر الثقيلة مثل (الزرنخ ، الكروم ، الرصاص ، الكاديوم) في المياه الطبيعية وذلك باستخدام قرص من مركب راتنجي كليتي. وكان قطر القرص الراتنجي بحدود 6 ملم وكان الماء النموذج المستخدم. واستخدم في هذا البحث حامض النتريك بتركيز 0.2 M وتم تحديد تراكيز تلك العناصر الثقيلة في المياه.

