

A Semi-Automated Resin Concentration Method for the Preconcentration of Trace Metals in Fresh Water, Prior to Atomic Absorption Analysis

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Abstract

A semi-automated method, suitable for the preconcentration of trace metals in fresh water, was developed for use in routine trace metal analysis. A peristaltic pump was used to control the flow of water samples through columns of a cation exchange resin (Amberlite IR-120/H), the samples being stabilized with ascorbic acid (0,5 g/l) at a pH of 2,5 during the sorption stage. The metals concentrated were chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead.

Introduction

The analyst is often faced with the problem that the metal to be determined is present at a concentration below the limit of detection of the available instrumentation, for instance where a flame atomic absorption apparatus is used to analyze relatively unpolluted water samples. This difficulty can be overcome by using a more sensitive analytical technique (e.g. furnace atomic absorption), or alternatively by using some enrichment procedure to increase the concentration of the particular trace metal to a level which can be analyzed with flame atomic absorption. The metals chromium, cobalt, nickel, copper, cadmium and lead are generally present at concentrations below the limit of detection of flame atomic absorption in unpolluted river or dam water, while ubiquitous iron and manganese seldom require enrichment prior to analysis.

Many enrichment techniques have been described, such as chelation/extraction procedures and ion exchange procedures (Watling and Watling, 1976). The authors found that manual chelation/extraction techniques were unsuitable for the routine analysis of a large number of samples due to the difficulty in achieving reproducibility during the analytical manipulations, as well as the problem of obtaining good recoveries with real samples, as opposed to synthetic samples. Tweenen and Knoeck (1976) describe the latter problem with a diethyldithiocarba-

mate chelation and isoamyl alcohol extraction technique used on river water samples.

Automated operations inherently have a better reproducibility than manual operations, and therefore it was decided to automate the concentration step in the sample enrichment procedure. Since the simplicity of a resin concentration technique (Samuelson, 1963b) lends itself more readily to automation than a chelation/organic solvent extraction procedure, a resin technique was chosen for this purpose.

Experimental

The basis of the resin concentration method described here is the use of a peristaltic pump to control the flow of water samples through resin columns attached in parallel to the pump, thus making possible the simultaneous sorption/elution of a set of samples.

The instrumentation used was a Jarrell-Ash 810 atomic absorption spectrophotometer for the atomic absorption measurements, and the peristaltic pump was a Technicon Auto Analyzer II proportioning pump.

Reagents used were analytical grade except where stated otherwise. The deionised water was prepared by passing distilled water through a Milli-Q deioniser, which delivers deionised water with a conductivity of less than 0,01 mS/m. The glass and plasticware were precleaned by washing in sequence with a detergent, distilled water, deionised water, 0,5 M hydrochloric acid for 24 h (a deviation from the normal procedure of rinsing with 8M nitric acid (American Public Health Assoc., 1976) or 4M nitric acid (Bowditch, *et al.*, 1976)) and lastly 4 rinses with deionised water.

The cation exchange resin Amberlite IR-120/H was used in the free acid form in order to allow preconcentration of the readily hydrolyzable element iron. The resin was cleaned by washing 3 times with 4M hydrochloric acid alternated with deionised water (Samuelson, 1963). Twenty six resin columns

were prepared by packing 2 ml washed resin in 7 mm i.d. clear tygon tubing with cotton wool pads at each end (Fig. 1).

A twenty six channel peristaltic pump was used to pump the contents of twenty five samples and one blank simultaneously through the resin columns, using 1,6 mm i.d. polyethylene for transmission lines and 0,86 mm i.d. tygon tubing in the peristaltic pump, which gave a constant flow rate of 0,42 ml/min and a flow through time in the resin column of just under 5 min.

Before use, the resin columns were freed, if necessary, of any entrapped air by detaching the columns from the flow lines and aspirating deionised water rapidly through each column with a syringe. The resin columns were then cleaned by pumping 12 ml 3M hydrochloric acid (redistilled AR) followed by 12 ml deionised water through the columns.

The water samples analyzed were treated as follows: The samples, collected in precleaned polyethylene bottles and preserved with concentrated nitric acid (5 ml/l), were filtered in the laboratory through a 0,45 μm pore size membrane filter to remove particulate matter (US Environmental Protection Agency, 1974). Ascorbic acid (0,5 g/l) was then added, and the pH adjusted to between 2,0 and 2,5 with concentrated ammonia solution using pH indicator paper — a glass rod being used to transfer a drop of the sample to the pH indicator paper. The samples were then pumped through the cleaned resin columns (at 0,42 ml/min) to sorb the metals onto the resin. The time necessary to pump 500 ml sample volumes through the resin columns was just under 20 h. With subsequent elution of the sorbed metals to a volume of 50 ml, a concentration factor of 10x was obtained. The volume of each sample passed through the resin columns was measured to determine the exact concentration ratio.

To elute the metals from the resin columns, 25 ml 3M hydrochloric acid (redistilled AR) followed by 12 ml deionised water was pumped through each column, the eluate being collected in 50 ml volumetric flasks. Concentrated ammonia solution (3,5 ml) was then added to the eluate in each 50 ml volumetric flask to reduce the excessive acidity, which was found to produce noisy signals in the subsequent atomic absorption analysis. The pH of the eluate after the addition of ammonia solution was found to be less than 2. The eluate was made up to 50 ml with deionised water and transferred to 50 ml

polyethylene bottles until analysis by flame atomic absorption spectroscopy.

The resin columns were then regenerated for the next batch of samples with 25 ml 3M hydrochloric acid (redistilled AR).

Evaluation of the Method

To test the method, recovery tests were done on tap water samples taken from Roodeplaat Dam (which has around 260 mg/l dissolved salts). In the first test, aliquots of acidified and filtered water (sample no. 1) were analyzed as described above. The results are presented in Table 1, which illustrates the precision of the method. To ascertain the accuracy of the method, aliquots of the original sample were individually spiked with 50 $\mu\text{g/l}$ amounts of the various metal cations, preconcentrated and analyzed, and the percentage metal recovered calculated by subtracting the mean concentration in the raw sample from the concentration found in the spiked aliquot, and expressing the difference (which is the metal recovered) as a percentage of the amount of metal added (50 $\mu\text{g/l}$ in this case). The seven metals determined showed mean recoveries between 91% and 97% (Table 2).

To test the method over a range of concentrations, a raw sample (sample no. 2) was used which on analysis showed only iron in detectable concentration ($41,1 \pm 0,6 \mu\text{gFe/l}$), the other metal cations being below their respective limits of detection: Cr < 3 $\mu\text{g/l}$; Mn < 0,5 $\mu\text{g/l}$; Co < 1 $\mu\text{g/l}$; Cu < 0,5 $\mu\text{g/l}$; Zn < 2 $\mu\text{g/l}$; Cd < 0,1 $\mu\text{g/l}$; Pb < 6 $\mu\text{g/l}$.

Fifteen aliquots of this sample were then individually spiked with measured amounts (from 20 to 160 $\mu\text{g/l}$) of the various metal cations and these aliquots then preconcentrated and analyzed. Recoveries were then calculated as described in the first test, except that where the concentration of metal in the raw sample no. 2 was below the detection limit, the value was taken as zero. As the concentrations of the metals (other than iron) in sample no. 2 may have been near the detection limit and not zero, this places uncertainty on the absolute values of the recoveries calculated for the low spikes. The original

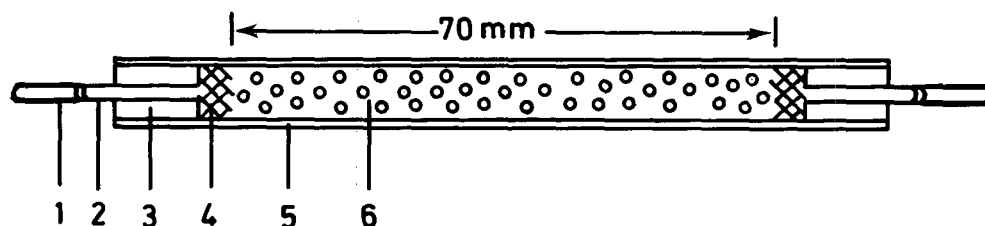


Figure 1

The Resin Column

- (1) 1,6 mm i.d. tygon (2) 1,4 mm i.d. tygon (3) tygon sleeve (4) cotton wool plug (5) 7 mm i.d. tygon
(6) 2 ml Amberlite IR — 120/H

TABLE 1
CONCENTRATIONS ($\mu\text{g/l}$) OF METALS IN ALIQUOTS OF SAMPLE NO. 1, AND MEAN CONCENTRATION (\bar{x}) \pm ONE STANDARD DEVIATION (S). RESIN CONCENTRATION FACTOR WAS 11,4

Element	Mn	Fe	Co	Ni	Cu	Cd	Pb
Aliquot 1	—	8	2,7	4,5	6,3	0,7	17,0
2	0,63	10	3,9	5,0	6,4	0,7	16,3
3	0,59	13	3,2	4,3	6,1	0,8	16,3
4	0,63	12	3,4	4,0	5,7	0,7	18,5
5	0,61	7	3,8	4,9	5,6	0,9	15,9
$\bar{x} \pm S$	$0,62 \pm 0,02$	10 ± 3	$3,4 \pm 0,5$	$4,5 \pm 0,4$	$6,0 \pm 0,4$	$0,8 \pm 0,1$	17 ± 1

TABLE 2
RESULTS OF SPIKING ALIQUOTS OF SAMPLE NO. 1 WITH 50 $\mu\text{g/l}$ AMOUNTS OF THE VARIOUS METALS. CONCENTRATIONS ARE IN $\mu\text{g/l}$ AND RECOVERIES IN %. THE ERROR GIVEN FOR THE MEAN RECOVERY IS ONE STANDARD DEVIATION. RESIN CONCENTRATION FACTOR WAS 11,4

Element	Mn	Fe	Co	Ni	Cu	Cd	Pb
Raw sample:	0,6	10	3,4	4,5	6	0,8	17
add 50 $\mu\text{g/l}$:	50,6	60	53,4	54,5	56	50,8	67
Aliquot 1							
found	46,2	58	48,1	50,5	52,5	48,0	64,6
subtract raw	45,6	48	44,7	46,0	46,5	47,2	47,6
$\div 50 = \text{Recovery}$	91%	96%	89%	92%	93%	94%	95%
Aliquot 2							
found	44,6	54	—	50,5	51,5	—	—
subtract raw	44,0	44	—	46,0	45,5	—	—
$\div 50 = \text{Recovery}$	88%	88%	—	92%	91%	—	—
Aliquot 3							
found	47,2	54	49,2	52,1	52,2	48,8	64,5
subtract raw	46,6	44	45,8	47,6	46,2	48,0	47,5
$\div 50 = \text{Recovery}$	93%	88%	92%	95%	92%	96%	95%
Aliquot 4							
found	49,4	54	50,1	51,1	52,0	49,4	67,3
subtract raw	48,8	44	46,7	46,6	46,0	48,6	50,3
$\div 50 = \text{Recovery}$	98%	88%	93%	93%	92%	97%	101%
Aliquot 5							
found	48,8	58	50,3	52,7	52,7	50,6	66,2
subtract raw	48,2	48	46,9	48,2	46,7	49,8	49,2
$\div 50 = \text{Recovery}$	96%	96%	94%	96%	93%	100%	98%
Mean Recovery:	$93\% \pm 4$	$91\% \pm 4$	$92\% \pm 2$	$94\% \pm 2$	$92\% \pm 1$	$97\% \pm 3$	$97\% \pm 3$

TABLE 3
RECOVERIES (%) OF 20 TO 160 $\mu\text{g/l}$ SPIKES ON SAMPLE NO. 2. THE ERROR GIVEN FOR THE MEAN RECOVERY IS ONE STANDARD DEVIATION. RESIN CONCENTRATION FACTOR WAS 9.06

Element	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Aliquot $\mu\text{g/l}$ added									
1 20	89	90	73	110	94	94	114	108	83
2 20	89	96	79	108	91	89	105	104	94
3 20	100	96	62	105	99	83	100	105	94
4 40	83	93	73	97	97	90	99	97	91
5 40	86	95	70	97	95	95	101	101	91
6 40	94	93	56	94	97	86	95	94	94
7 80	105	91	79	104	103	93	103	98	106
8 80	88	85	74	95	94	90	101	96	101
9 80	86	82	72	86	90	83	93	90	87
10 120	92	92	83	92	93	87	93	96	96
11 120	90	88	83	90	92	86	98	94	92
12 120	91	89	78	94	95	87	107	93	99
13 160	—	76	71	—	89	81	90	—	—
14 160	97	89	82	97	95	87	92	99	110
15 160	94	95	88	100	98	90	97	96	109
Mean Recovery	92 \pm 6	90 \pm 6	75 \pm 8	98 \pm 7	95 \pm 4	88 \pm 4	99 \pm 6	98 \pm 5	96 \pm 8

sample no. 2 was not stripped of metals prior to spiking as this would have changed the sample so that it would no longer represent a natural matrix. The recoveries found with sample no. 2 are given in table 3, the mean recoveries for eight of the elements analyzed lying between 88% and 99%, with iron having a somewhat low recovery for this sample of 75%.

The tests show that the method gives good recoveries for chromium, manganese, cobalt, nickel, copper, zinc, cadmium and lead. The recovery for iron was good on sample no. 1 (91% recovery), but rather low on sample no. 2 (75% recovery). The reason for this discrepancy is unexplained, and it illustrates the difficulty which is often experienced in achieving good recoveries on real samples.

Discussion and Conclusion

The semi-automated resin concentration method described here is useful for the preconcentration of a large number of samples, does away with the tedium characteristic of manual enrichment techniques, and gives good recoveries for the nine metals tested (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb).

Difficulty was experienced in obtaining consistent results for iron, but it was found that with the addition of ascorbic acid to the samples, prior to sorption onto the resin, more consistent results were obtained. Ascorbic acid serves as a complexing agent to counteract hydrolysis of iron, which difficulty has

been solved by others using malonic acid (Tetsuo Uchida, *et al.*, 1977) or citric acid (Halldor Armannsson, 1977).

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