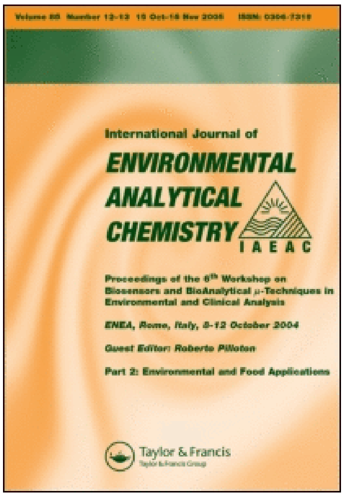

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The Use of Activated Charcoal for Preconcentration of Trace Heavy Metals from River Water in their Analysis by Thermal-Neutron Activation

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The Use of Activated Charcoal for Preconcentration of Trace Heavy Metals from River Water in their Analysis by Thermal-Neutron Activation

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The use of activated charcoal in the separation of some trace heavy metals from water and subsequent analysis by neutron activation has been investigated. The recovery is quite good for As, Cr, Hg and Zn at pH between 8 and 8.5 but poor for Co, Cu, Cd and Sb. Co, Cu and Zn are efficiently adsorbed after complexation with ammonium-pyrrolidinedithiocarbamate at pH 4.5 and 6.5. In both cases about 0.5 g activated charcoal is sufficient for 1 litre water. The procedure is applied to the determination of As, Cr, Hg, Cu, Co and Zn in the polluted Ogba River, the present main source of tap water supply to Benin City. The measured high levels of these metals especially As, Cr and Cu are attributed to contamination due to the effluents from a nearby Wood Preservative Treatment Factory.

KEY WORDS: Activated charcoal, preconcentration, trace-metals, water.

INTRODUCTION

In surface waters the concentration of various elements may nowadays be increased far beyond natural values due to the release of industrial, agricultural and domestic waste water. The presence and fate of these elements, especially the heavy metals, in natural and drinking waters in relatively high concentrations and their chronical toxicity have become priority areas of research in the chemistry of marine and fresh water ecosystems. Much interest has therefore been shown in the analysis of water for trace elements using among others the technique of neutron activation analysis (NAA).

Preliminary concentration procedures are usually required in trace element analysis of water samples, since in various natural waters most of the heavy metals are present in low concentrations even in areas associated with particular heavy metal pollution burdens. The preconcentration procedures, used by some authors include liquid extraction with complexing agents,[1,2] use of chelating resin columns,[3-5] evaporation to dryness,[6] evaporation followed by co-precipitation with $Al(OH)_3$, $Fe(OH)_3$ and PbS,[7,8]. Some of these methods have their limitation and disadvantages, depending on the trace elements of interest. In a previous study[9] rain water samples were preconcentrated by freeze evaporation using a lyophilizer. The method was quite efficient but it took several hours to concentrate a litre of water to about 15 ml.

The heavy metal content in water may be distributed between the dissolved state and suspended particles of biological and organic nature. Some authors have suggested the use of activated charcoal[10] and manganese(IV) oxide[11] for preconcentration of trace elements from water. The adsorption of metal complexes on activated charcoal is also known.[12] The procedure presented in this paper consists of the use of activated charcoal with and without complexing agents for preconcentration of some heavy metals from water and subsequent analysis by NAA.

EXPERIMENTAL

Chemicals and reagents

The comparator standard solutions for NAA and the stock solutions for preliminary adsorption studies were prepared by dissolving the metal salts, mainly acetates and nitrates in deionized water and the oxides of As, Hg and Sb in nitric acid. Two types of activated charcoal, AC: BDH, 33187 and BDH, 33033 (BDH Chemical Ltd., England), used for the analysis were dried for several days over P_2O_5 in a desiccator. Their trace metal content was checked by NAA of aliquots of the two samples. Both types were found to contain very small or no traces of the metals of interest. The results

TABLE I

Trace metal content of the activated charcoal used for the analysis ($\mu g/g^{-1}$ dry weight).

Metal	BDH, 33187	BDH, 33033
As	<0.001	<0.001
Cd	<0.001	<0.001
Co	0.061 ± 0.003	0.07 ± 0.003
Cr	0.58 ± 0.045	0.61 ± 0.044
Cu	<0.02	<0.02
Fe	103 ± 9.4	106 ± 8.7
Hg	0.014 ± 0.001	0.017 ± 0.001
Sb	0.074 ± 0.005	0.083 ± 0.005
Zn	0.16 ± 0.014	0.21 ± 0.014

of the analysis are shown in Table I. All the chemicals and reagents including ammonia and ammoniumpyrrolidinedithiocarbamate, APDC (Merck, Darmstadt) were of analytical grade.

Recovery of trace metals from water by adsorption on AC

A litre of deionized water was spiked with accurately known amounts of the metals in one or two ml solution. The spiked metal concentrations were comparable to the trace metal concentrations reported in the literature for various surface waters.[13] Also, a known weight of AC was added and the solution was adjusted to a desired pH. After vigorous stirring for different periods of time, the AC was separated by filtration through a porcelain Buchner funnel using Whatman 40 filter paper (diam. 5.5 cm). The filter paper was then carefully transferred in a compacted form into an irradiation vial, which was enclosed in another capsule for irradiation. In the second procedure, the spiked water was treated with the same amount of AC and 0.2 g APDC and processed as described after adjusting the pH.

Influence of stirring time, pH and amount of activated charcoal

The effect of stirring time, pH and amount of AC on the adsorption of the trace metals was investigated. The stirring time in each case was varied from 10 to 30 min at pH values ranging from 5 to 9. The AC was filtered and analyzed in the same manner for any varied conditions to determine the recoveries of the trace metals.

NAA method

The filtered activated charcoal samples and the comparator standard solutions of the metals of interest were irradiated in the rotary specimen rack tubes of the TRIGA MARK I reactor of the University of California, Irvine at a thermal-neutron flux of $1.0 \times 10^{12}\,\mathrm{n\,cm^{-2}\,sec^{-1}}$ for 3 hours. The samples and standards were counted with a $90\,\mathrm{cm}^3$ coaxial Ge(Li) detector, connected to a 4096-channel pulse-height analyzer, for 15 or 30 min after decay periods of between one day and 2 weeks, depending on the half-life of radionuclide of interest. For the determination of Cu (as ^{66}Cu, half-life = 5.1 min) each sample, as well as the standard, was irradiated for 30 sec (one at a time) using the pneumatic tube transfer system of the reactor at a neutron flux of $2.5 \times 10^{12}\,\mathrm{n\,cm^{-2}\,sec^{-1}}$. After a decay time of 20 min, each was counted for 2 min. Corrections for flux variations, decay and photopeak baselines were appropriately effected. The data on the (n, γ) radionuclides and their measured gamma-ray peaks are given in Table II.

TABLE II

Data on (n, γ)-radionuclides and the measured gamma-ray peaks.

Element	(n, γ)-radionuclide	Half-life	Measured γ-energy/ energies (keV)
As	^{76}As	26.3 hr	559, 657
Cd	^{115}Cd	53.4 hr	528
	^{115m}In	4.5 hr	336
Co	^{60}Co	5.24 yr	1332.1
Cr	^{51}Cr	27.8 d	320
Cu	^{66}Cu	5.1 min	1039
Hg	^{197}Hg	65 hr	69 and 77.5
Fe	^{59}Fe	45.1 d	1098.6, 1291.5
Sb	^{122}Sb	2.75 d	564
Zn	^{69m}Zn	13.8 hr	438.7

Analysis of Ogba River water samples

The river water samples were collected from 3 locations on the river, chosen as follows: (a) near point source of Ogba river, where the main City water work is located (b) downstream near the Wood Treatment factory, about 2 km from the source and (c) at Ogbaneki, about 4 km downstream from the factory. The water samples were stored in 2-litre polyethylene bottles, previously cleaned with conc. HNO_3 and rinsed with deionized water. The pH of the samples was between 4.5 and 6.5. The samples were filtered through 0.45 μm pore-diameter membrane filter. For the determination of As, Hg and Cr about 0.5 g AC was added to 1 litre water and processed as previously described. Another 1 litre portion was similarly treated with AC and 0.2 g APDC for the measurement of Co, Cu and Zn levels. In the case of these water samples the filtered AC was washed several times with deionized water to remove any Na, Cl and Br, which might be adsorbed on it. This is necessary because the analysis of surface water by neutron activation can be limited by poor precision of determination due to interferences by high ^{24}Na and ^{82}Br activity.

RESULTS AND DISCUSSION

Recovery of trace metals from water samples

The results of the adsorption experiments are presented in Tables III and IV. The metals As, Cr, Hg and Zn were quantitatively removed from the spiked water using AC. Average percentage recoveries of about 97, 98, 95 and 94 were achieved for As, Cr, Hg and Zn respectively at pH between 8 and 8.5. At lower pH values the recoveries were not so good, showing strong dependence of adsorption on the pH of the solution. Under the same conditions the recoveries of Cd and Sb were particularly very poor (between 23 and 33%). The results for Co and Cu were not satisfactory (less than 60 and 70% for Co and Cu respectively).

In Table IV the results show that the addition of APDC, a complexing agent, was responsible for almost complete separation of Co, Cu and Zn from the water samples within the pH range of 4.5 to 6.5. The recovery of these metals was not necessarily dependent on the pH of solution. However, the effect of pH, higher than 6.5

TABLE III

pH-dependence on the percentage recovery of trace metals from spiked deionized water using activated charcoal (0.5 g activated charcoal in 1 litre water; stirring-time between 20 and 30 min).

Metal	Added, $\mu g.l^{-1}$	Percentage recovery on activated charcoal				
		pH 5.5	pH 6.5	pH 7.5	pH 8	pH 8.5
As	68.5	63.7	71.3	89.4	97.8	96.4
Cd	30.5	18.1	16.7	20.8	22.3	23.1
Co	8.7	43.6	46.4	51.4	58.7	57.9
Cr	175	66.8	68.0	90.5	97.7	98.5
Cu	205	47.5	57.4	60.4	63.6	68.1
Hg	6.75	68.1	74.6	88.7	94.3	95.4
Sb	41	23.6	24.4	30.2	33.1	32.6
Zn	64.7	76.7	75.0	87.8	94.0	93.1

TABLE IV

pH-dependence on the percentage recovery of trace metals from spiked deionized water using activated charcoal in presence of APDC. (0.5 g activated charcoal and 0.2 g APDC in 1 litre water, stirring-time 20–30 min).

Metal	Added, $\mu g.l^{-1}$	Percentage recovery				
		pH 4.5	pH 5	pH 5.5	pH 6	pH 6.5
Cd	30.5	15.7	15.4	19.1	23.7	25.2
Co	8.7	92.8	96.8	100	99.6	100
Cu	205	93.1	94.7	98.6	100	98.8
Sb	41	23.4	24.8	24.1	26.0	26.7
Zn	64.7	95.6	96.0	97.8	99.4	98.7

was not further investigated. It has been suggested that activated charcoal may be a good adsorbent for some heavy metals and their complexes. This may account for the quantitative recovery of Co, Cu and Zn by complexation with APDC. This is also evident, when their recoveries shown in Table IV are compared with those in Table III. The results for Cd and Sb were still poor on addition of APDC. Perhaps, their recoveries can be improved, if suitable complexing agents are used in the same adsorption matrix. The effect of the amount of adsorbent and stirring time on recovery showed that about 0.5 g AC and a stirring time of 20–30 min was sufficient for 1 litre water.

The advantage of this preconcentration method is the elimination of interferring ^{24}Na, ^{82}Br and ^{38}Cl activities, usually encountered in the analysis of fresh water and seawater for trace metals by neutron activation. Na, Br and Cl are very poorly adsorbed on Ac. Any traces of them can, however, be almost completely removed by washing the adsorbent several times with deionized water. Secondly, the separation of the trace metals by this simple procedure is achieved in less than one hour. It can be carried out immediately after sample collection. Thirdly, any possible contamination of samples and, more importantly, loss of volatile elements are minimized.

Trace metal levels in Ogba River

The metal concentration levels measured in Ogba river water from 3 locations are presented in Table V. Their concentration ranges for three replicate determinations, as well as their average values, are also given. The relative standard deviations (1σ) for the metal concentrations varied in the range of 4.6 to 10%. It should be noted that, where two gamma-ray energies (Table II) have been used to measure the concentrations, such as in the cases of As, Cd and Fe, the difference between any two values in each case was small. However, the lower values have been reported.

The concentrations of all metals determined especially As, Cr and Cu are relatively very high, when compared with their mean values for fresh water reported by Bowen.[13] The Ogba river, like other Nigerian rivers flowing through towns and villages, receives large quantities of rubbish of complex compositions and various untreated wastes, ranging from domestic to industrial. Other factors such as floods from rain storms and laundry operations, being carried out in this river at various points, can also contribute to the high levels of these metals. The exceptionally high levels of As, Cr and Cu, measured in the samples collected from locations I and II (Table V), can be attributed to effluents from the Wood Treatment factory, located near the river. Salts of As, Cr and Cu are used in soluble formulations for long-term preservation of timber against insect and fungal attacks. The factory therefore provides a potential distribution source of these metals into the general environment, especially this

TABLE V

Results of replicate analysis of Ogba River water samples for As, Co, Cr, Cu, Hg and Zn ($\mu g.l^{-1}$).

	Location I		Location II		Location III	
Metal	Concentration range for 3 runs	Average	Concentration range for 3 runs	Average	Concentration range for 3 runs	Average
As	65.4–74.3	68.9	60.1–66.4	63.3	14.8–16.83	15.58
Co	3.74–5.4	4.48	3.14–4.7	3.98	2.74–3.67	3.1
Cr	138–147	142	123–136.4	130	87.4–94.0	89.8
Cu	267–304	286	187–258	215.3	68.4–74.5	71.4
Hg	5.64–8.72	6.92	5.84–7.83	6.63	2.45–3.43	2.9
Zn	84.7–107.5	96.2	87–116.4	102.5	18.4–22.3	20.5

Location I = samples collected near the Wood Treatment Factory.
Location II = samples collected at Ogbaneki, about 4 km downstream from location I.
Location III = samples collected at the source of Ogba river, where the main City Water Work is located.

river, by way of spills and leakages of the treating chemicals. as well as drainages from the treated wood. From the results obtained for the samples collected from the locations I and II, it can be seen that the trace metal composition of this river has not changed very significantly within the short distance. The concentrations measured in samples from the point source of the river (location III) are comparatively low, showing less contamination by industrial and other effluents.

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References

1. R. R. Brooks, B. J. Presley and I. R. Kaplan, *Talanta* **14,** 809 (1967).
2. J. D. Kinrade and J. C. Van Loon, *Anal. Chem.* **46,** 1894 (1974).
3. C. Lee, N. B. Kim, I. C. Lee and K. S. Chung, *Talanta* **24,** 241 (1977).
4. T. M. Florence and G. E. Batley, *Talanta* **23,** 179 (1976).
5. B. Holynska, *Radiochem. Radioanal. Letters* **17,** 313 (1974).
6. Y. Kusaka, H. Tsuji, Y. Fujimoto, K. Ishida, T. Mamuro, T. Matsunami and A. Mizohata, *Bull. Inst. Chem. Research*, Kyoto Univ. **58,** 171 (1980).
7. S. Nagatsuka, Y. Tanizaki and Y. Okano, *Radioisotopes* **23,** 693 (1974).
8. S. Nagatsuka and Y. Tanizaki, *Radioisotopes* **25,** 375 (1978).
9. C. L. Ndiokwere, *Radioisotopes* **31,** 583 (1982).
10. E. Jackwerth, J. Lohmar and G. Wittler, *Z. Anal. Chem.* **266,** 1 (1973).
11. V. N. Sastry, T. M. Krishnamoorthy, G. R. Doshi and T. P. Sarma, *Ind. J. Chem.* **12,** 200 (1974).
12. M. Arnac and G. Verboom, *Anal. Chem.* **46,** 2059 (1974).
13. H. J. M. Bowen, *Environmental Chemistry of the Elements* (Academic Press, London, New York, 1979) 1st ed. pp. 16–17.