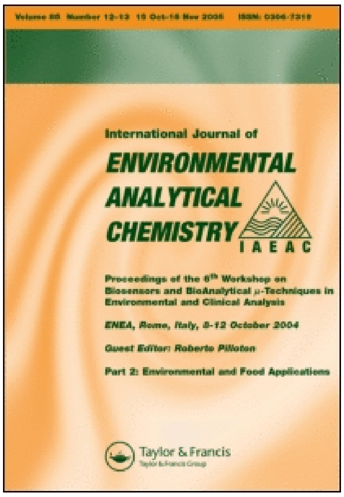

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Determination of the Speciation of Chromium from a Bicycle Factory Discharge

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The discharge from a bicycle factory in Dar-es-Salaam was analysed for dissolved trace metals so as to monitor what was being introduced onto the environment. An X-ray Fluorescence Spectrophotometer with a Si (Li) detector connected to a multichannel analyser Canberra 40 series was used for the analysis. Computation of the peaks and results was done by a Professional Deck 350 computer. The elements contained in the discharge were Ca (596 ppm), Ti (369 ppm), Cr (11 ppm), Zn (0.98%) and Sr (73.5 ppm). Further analysis of the speciation of chromium revealed that there was Cr(III) (9 ppm) and Cr(VI) 2 ppm. The level of Cr(VI) was considered too high considering its toxicity.

KEY WORDS: Chromium(VI), speciation, preconcentration, X-ray fluorescence, spectrometry, waste water.

INTRODUCTION AND THEORY

Trace elements in the aquatic environment are essential for the metabolism of plants and animals. Among the trace elements, chromium has been identified as an active and essential element in the retention of sugars.[2] Chromium has several oxidation states i.e. Cr(III), Cr(IV) and Cr(VI). Of these Cr(III) and Cr(VI) are the most common.[7] In aquatic systems the probable species are $CrO_{4^=}$, $HCrO_{4^-}$, $Cr^{3+}(aq)$ and Cr_2O_3, nH_2O.[9] In sea water $CrO_{4^=}$ is the thermodynamically stable species.[8,9,12]

Chromium(VI) is more easily absorbed into tissue than other oxidation states[6] and it is also highly poisonous.[7] Due to its toxicity several scientists took an interest on the speciation of chromium in natural aquatic systems.[3,5,6,13,14,17]

Determination of chromium in aquatic systems has been done by atomic absorption spectrometry (AAS) by several scientists.[2,8,10,12,15] Due to matrix effects the element has always had to be extracted from sea water by: (a) complexation with acetylacetone/chloroform mixture;[2,15] (ii) solvent extraction with methyl isobutyl ketone (MIBK);[10] (iii) coprecipitation by ferric hydroxide.[8,12] Leyden and Channel[14] determined microgram quantities of chromium by X-ray fluorescence after chelation by an ion-exchange resin and reduction of Cr(VI) to Cr(III) by sodium bisulphite. Differential pulse polarography and chemiluminescence has also been used in the determination of chromium.[6,13]

Of all the above methods used determination by AAS is commonly used due to its high sensitivity, lack of interference and rapidity with which analyses can be done. Preconcentration is done by ferric hydroxide and a chelex resin. The solvent extraction by ammonium dithlocarbamate (APDC) and MIBK is also popular especially when the samples are small. In this work ferric hydroxide was used for coprecipitation and analysis done by an X-ray Fluorescence Spectrophotometer.

MATERIALS AND METHODS

Experimental

Sample collection The water sample was collected by a plastic carboy which had previously been soaked in 2 m HNO_3 acid for 24 hours. The container was immersed in the pool of the water until full, stoppered and taken to the laboratory for immediate analysis.

Preparation of reagents Iron(III) solution was prepared by adjusting 0.01 M iron(II) ammonium sulphate solution to pH 8 (PTI-15 Digital pH meter) with ammonium hydroxide (10%) and shaking for 12 hours to oxidize the iron(II) hydroxide. Iron(II) hydroxide was prepared by adding 1 ml of 10% ammonium hydroxide to 50 ml of iron(II) ammonium sulphate.

Co-precipitation An aliquot of 140 ml of the water sample was treated with 1 ml of 0.01 M iron(III) hydroxide at pH 8 then shaken for 1 hour. After shaking the sample was filtered through a 0.45 μm Nucleopore membrane filter then dried in a dessicator before the analysis. Analysis was done by an X-ray Fluorescence Spectrophotometer (Commodore). The iron(III) hydroxide precipitated Cr(III) only. In order to precipitate chromium(VI) iron(II) hydroxide 1 ml (0.01 m) was added to a 140 ml aliquot and the mixture shaken for 1 hr then filtered as above. During the shaking Cr(VI) was reduced to Cr(III) while the iron(II) was being oxidized to iron(III). The difference in the amount of chromium obtained from the two aliquots was the concentration of chromium(VI).

Instrumental

An X-ray Fluorescence Spectrophotometer was used in the analysis. The detector used was a Si(Li) (area 78.5 mm^2) detector using 109_{cd} as the source of X-rays for 5,000 seconds irradiation. The multichannel analyser was Canberra 40 series which was connected to an online computer (Professional Deck 350). The energy at full width half maximum (FWHW) for the 55_{Fe} peak was 165 ev.

RESULTS AND DISCUSSION

Results are summarized in Tables I and II. Of all the metals found in the discharge it is only chromium(VI) which is of environmental concern in view of its toxicity. On the basis of standards set in 1968[16] water with a Cr^{6+} concentration in excess of 0.05 ppm is rejected for domestic use. The discharged treated water was not for human use. However, the tributary from the factory passes via open land where there are grazing cattle and then finds its way into the sea, hence it is important to know the concentration of Cr^{6+}.

Chromium being a heavy metal it is bound to be deposited in the sediments then remobilized with varying pH and Eh conditions; in which case the amount of chromium reaching the sea could be minimal. One way of determining whether there was a decrease in dissolved chromium with increased distance from the discharge point is to analyse the sediments. Unfortunately this was not done due to

TABLE I

Concentration of metals in the discharge

Element	Concentration
Ca	596 ppm (±0.006)
Ti	369 ppm (±0.001)
Cr	11 ppm (±0.001)
Zn	0.97% (0.0008)
Sr	73.5 ppm (±0.0002)

TABLE II

Concentration of Cr species

Cr type	Fe type	Average concentration
Cr (total)	$Fe(OH)_2$	11 ppm
Cr(III)	$Fe(OH)_3$	9 ppm
Cr(VI)	$Fe(OH)_2$	2 ppm

the lack of a freeze drier since wet sediment samples for X-ray analysis have to be freeze dried. More work is therefore required especially on the Cr trapped in sediments.

At this juncture it can only be concluded that the level of Cr^{6+} discharged is of environmental concern. The degree of the pollution can only be verified after a thorough analysis of the amounts and speciation of chromium reaching the sea.

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