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Speciation of Cu and Cr in the aqueous environment by Spectroscopic and Voltommetric techniques.

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Summary: A study of the speciation of Cu and Cr in the aqueous environment of Cork is outlined. A comparison is made of spectroscopic and voltammetric techniques for the determination of Cu and Cr in water sample, and the meaning of the results are discussed.

Introduction

In recent years, detailed studies of the behaviour of trace metals in the aquatic environment have shown that a knowledge of their total concentration is insufficient to enable estimation of their impact therein. For this reason environmental scientists are becoming increasingly aware of the need for reliable methods, which can differentiate and determine the chemical forms of trace metals, especially the toxic heavy metals, in natural waters. Knowledge of the chemical state of trace metals in solution is important to understanding trace metal transport, reactivity and toxicity in aquatic environments. The common procedure for measuring the total concentration of a particular metal in a water sample, e.g. by atomic absorption spectrophotometry, can be very misleading because depending on the chemical forms of the metal, a water sample with a high total metal concentration and with a high degree of binding to organic molecules may in fact be less toxic than another sample with a lower total metal concentration but a low degree of binding to organics. For example most workers [1-3] have concluded that ionic copper is significantly more toxic towards aquatic organism than organically-bound copper, and the more stable copper complex, the lower is its toxicity. Steeman, Nielsen and Wium-Anderson [2] have suggested that deep seawater has a higher ratio of ionic copper to organically complexed copper than has surface water and that this could explain why upwelling water is unsuitable for the growth of phytoplankton, even though it is rich in nutrients [4]. The hypothesis has been supported by Barber and Ryther [4]. They found that the addition of a strong chelating agent to upwelling water considerably improved its productivity, and this was confirmed by Lewis et al. [5] who used EDTA to simulate a powerful natural chelating agent.

The degree of metal toxicity towards aquatic life with some exceptions decreass in the order mercury silver copper > cadmium > zinc > lead > chromium > nickel > cobalt [1]. It is often assumed that the dissolved metal is the form which is toxic to fish [6,7] on the basis that suspended or particulate metal forms (i.e. retained by a 0.45-μm membrane filter) are effectively unavailable to their gills. There is no doubt however, that ingested particles (e.g. sediment eaten with food) can contribute significantly to the body burden of heavy metals in fish, since these metals are rapidly absorbed from the stomach fluids [8]. With bottom feeding fish, sediments

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may be more important than water as a source of heavy metals.

In the area of water treatment, knowledtge of the chemical forms of the dissolved metals is important for efficient operation of the treatment plant. The efficiency of the treatment operation often depends on whether a metal is in ionic, complexed, colloidal or particulate form. Detailed information on the solution equilibria which cause metal speciation in natural water and on the measurement of trace metal speciation is given in a number of reviews [9-13].

In the aquatic environment three physical states are possible, broadly classified as the particulate, colloidal, and soluble. Copper could be distributed among all three phases. Particulate forms of copper might possibly include the oxide, sulphide, and malachite (Cu2(OH)$_2$Co$_3$) precipitates, as well as insoluble organic complexes and copper adsorbed on clays and on other mineral solids. Soluble matter is generally defined as that which passes a 0.45-μm membrance filter, and includes copper both as free cupric ion and as soluble complexes [14]. The colloidal matter includes polypeptide materials and some clays and metallic hydroxide precipitates. Different people have made different approach for the speciation of these chemical states.

The simpleast a.s.v. procedure for chemical speciation in water is the determination of labile (i.e. weakly complexed) and total metal concentration. Total copper, lead and zinc concentrations have been measured by a.s.v. after u.v. irradiation [15], persulphate oxidation [16] and heating with dilute nitric acid [17,18]. Acid exchangeable metal is sometimes used in place of total metal [19]. Labile metal is measured in slightly acidic solution, often with an acetate buffer by direct a.s.v. [13-18,20]. The results represent free metal ion plus metal dissociated at the electrode surface from complexes and colloids. The difference between total and labile metal has been called bound metal (i.e. strongly complexed), and as a crude approximation may be regarded as metal bound in inert complexes and other inert forms such as colloidal particles. Using a.s.v. techniques Florence and Batley [21] found that most of the copper present in sea-water is complexed with or on organic matter, and that a smaller percentage is associated with inorganic clloids. Equilibration studies with ionic copper -64 added to sea-water showed that after six hours only 50% exchange had taken place with the naturally present copper, thus confirming the inert nature of the bound fraction.

Stiff [14] presented a comprehensive scheme for the chemical speciation of dissolved copper in polluted fresh water. Stiff applied his scheme only to polluted water, containing 100-1000 μgdm^{-3} level of copper, i.e. copper concentrations two orders of magnitude higher than those found in most natural waters. Considerable modification would therefore be necessary before it could be used at natural levels of copper.

Determination of the ratio of two oxidation states of a metal in solution is a special case of speciation. In natural water the main interest in oxidation state determination has been directed towards chromium because of the high toxicity of Cr (vi) compared with Cr(111). Fukai and Vas [22] made use of the observation that Cr(111) is equantitatively co-precipitated on ferric hydroxide, where as Cr(vi) shows little tendency to co-precipitate.

They found that in most samples of sea-water studied the concentration of Cr(vi) exceeded that of Cr(111), whereas Chuecas and Riley [23], using a similar method, found the reverse to be true. Elderfield [24] pointed out that thermodynamic considerations predict that Cr(vi) should predominate in sea-water, in equilibrium with the atomosphere. However when he applied the method of Fukai and Vas [22] to samples of coastel sea-water he found that in fact most of the chromium was present as Cr(111).

Solvent extraction and atomic absorption determination have also been used for the speciation of copper and chromium. Matsunaga, Negishi and Fukase [25] used an atomic absorption method for speciation of copper in river and lake waters. Free copper was chelated with ammonium 1-pyrolidine carbodithioate (APDC) and extracted into metyl isobutyl ketone (MIBK) after digesting with acid the copper was back extracted and determined using an atomic absorption spectrophotometer. For organic copper, water is passed through a column of the anion exchange resin (Dowex 1x8) with a flow less than 10 ml minute^{-1}. After washing out the column with water, the copper complex is eluted by washing the column with 50 ml of nitric acid, and neutralization with aqueous ammonia the copper is determined by atomic absorption spectrophotometry.

Bergmann and Kardt [26] used the following method for the speciation of chromium in water. Cr (vi) is selectively chelated with ammonium 1-pyrolidine carbodithioate (pH 4.7-5.5), extracted with MIBK and is determined by atomic absorption spectrophotometer. The amount of Cr(111) is calculated by difference, after the determination of total chromium concentration by atomic absorption spectrophotometry.

In this paper the techniques of atomic absorption and electrochemistry are applied to the speciation of Cu and Cr in the aqueous environment of Cork, the latter element being investigated in a local "chromium spill", which also contained organic contimination.

Experimental

Apparatus

A Pye-Unicam atomic absorption spectrophotometer model SP 191 with a flameless atomizer model SP 9-01 was used for the determination of total and extractible copper and chromium. For determination of copper by anodic stripping voltammetry (a.s.v.) a PAR polarographic analizer model 174A in combination with model 303 stationary mercury drop electrode (s.m.d.e.) was used, while for the polargraphic determination of chromium and quinones a PAR model 364 polagraphic analyzer with dropping mercury electrode system was used. Voltammograms were recorded on a PAR model RE 0074 X-Y recorder. A Kent pH meter model EIL 7055 with glass electrode was used for pH measurements.

Reagents and Material

The following analytical reagent grade chemicals were used:- Sodium diethyldithiocarbamate (NaDED$_2$C), Diethylammonium diethyldithiocarbamate (DADC), Ammonium tetramethylenedithiocarbamate (ATDC), Ammonium 1-pyrrolidine-carbodithioate (APDC), 8-hydroxyquinoline, Dithizone cupferron, Acetylacetone 1-nitroso-2-napthol. Stock solutions (10^{-2}M) of all these chelating agents were prepared by dissolving the required weight of each compound in a small amount of Analar methanol and diluting to the required volume with triply-distilled water. Water for copper speciation studies was collected from the

College supply and for the chromium studies samples were collected from a local river, where the "chromium spill" had killed thousands of fish (date June 11, 1980).

Preparation of Supporting Electrolyte

(i) Ammonium citrate buffer (pH 3)

0.2M ammonium citrate buffer was prepared by dissolving 42 grams of citric acid in 800 ml of deionized water and the solution was adjusted to pH 3 by adding ammonium hydroxide, the volume was made to 1000 ml with deionized water.

Procedure

For the total copper and chromium determination by flame atomic absorption method the sample was directly aspirated into the flame (air-acetylene) and from the calibration plot, the quantity of copper and chromium in the unknown sample was calculated. For the total copper and chromium by the flameless system 20 ul of the sample was injected into the graphite furnace and the amount of copper and chromium in the unknown sample was obtained using the calibration plot prepared from standard copper and chromium solution.

For free copper determinations, 5 ml of the chelating agent (10^{-3}M) was added to a known amount of the sample, diluted to 50 ml in a 100 ml separating funnel. After adding 2 ml of MIBK, the solution was shaken mechanically for 10 minutes. The organic phase was then removed and 20 ul of this phase was injected onto the graphite furnace. In the same way standard copper solutions were extracted and a calibration plot was thus prepared prior to estimation of the unknown copper in the water sample.

For the determination of copper by d.p.a.s.v., 5 ml of water sample was taken in the sample cell to which 5 ml of ammonium citrate buffer solution were added. The solution was degassed by bubbling oxygen free nitrogen through for four minutes, after which a flow of nitrogen was maintained over the solution through the analysis. After 30s equiescent time, copper was deposited on a mercury drop (small) for two minutes and the d.p.a.s.v. was recorded on X-Y recorder. The concentration of copper in the water sample using the standard addition method utilizing the following formula [27].

$$Cu = \frac{i_1 v\ C_s}{i_2 v + (i_2 - i_1) V}$$

where

i_1 = stripping peak for sample

i_2 = stripping peak for sample + spike

v = volume of standard solution for spike

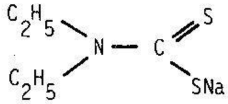
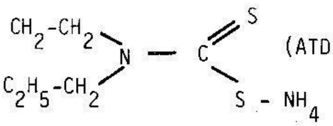
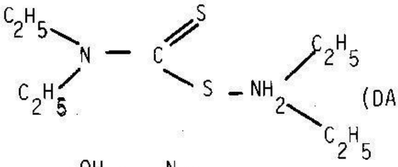
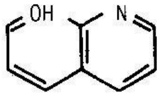
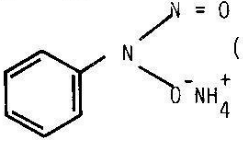
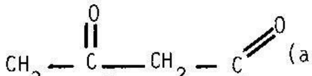
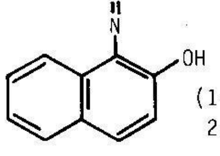
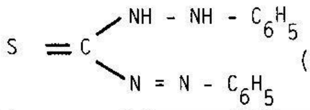
V = volume of sample taken

C_s = concentration of standard used to spike

Cu = concentration of unknown in the sample

For the determination of Cr(VI) by flameless atomic absorption spectrophotometry, the pH of the sample was adjusted to 4 and 5 1 of the chelating agent (1% APDC) added. After the addition of 5 ml of MIBK, the mixture was mechnically shaken for 10 minutes. After physically separating the two layers, 20 1 of the organic phase was

Table-1: The responses to different chelating agents for copper by flameless atomic absorption spectrophotometry

Chelating agent	concentration M	solvent	peak height cm^{-1}	Cu content $g\ dm^{-3}$
 (NaDEDC)	10^{-2}	H_2O	3.75	8.8
 (ATDC)	10^{-2}	H_2O	0.38	8.9
 (DADC)	10^{-2}	H_2O	0.25	5.8
 (8 hydroxyquinoline)	10^{-2}	Methanol	5.05	118.6
 (cupferon)	10^{-2}	H_2O	3.125	73.5
 (acetylacetone)	10^{-2}	H_2O	0.38	8.9
 (1-nitroso-2-napthal)	10^{-2}	Methanol	5.75	111.8
 (dithizone)	10^{-2}	Methanol	16.5	

injected onto the graphite furnace. In the same way standard Cr(VI) solutions were extracted and a calibration plot was thus prepared prior to estimation of the unknown Cr(VI) in the sample.

For the d.p.p. of total chromium, chromium was oxidized to Cr(VI) [27]. 20 ml of the working standards prepared in the supporting electrolyte (NaOH) were placed in the polarographic cell. Nitrogen was bubbled through the solution for five minutes, and a nitrogen atmosphere was maintained over the solution. The concentration of chromium in the sample was determined using the calibration plot prepared from the working standards.

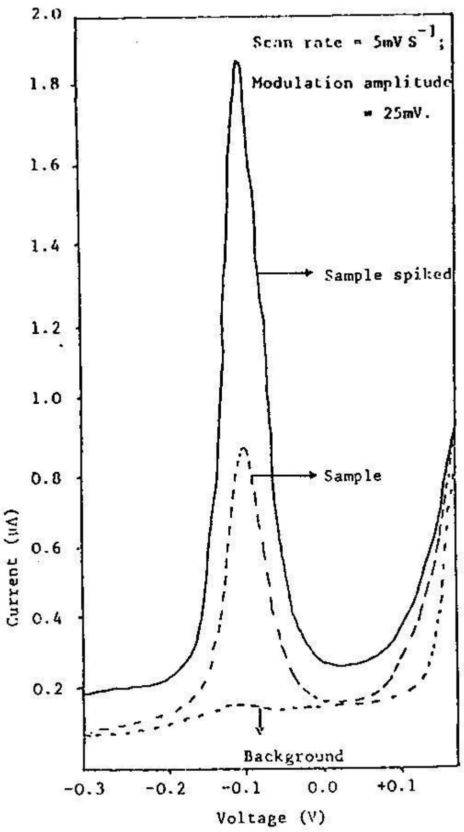


Fig. 1: The determination fo copper by differential pulse anodic stripping voltammetry using standard addition techniques.

Results and Discussion

1) Determination of copper by atomic absorption spectrophotometer

A number of chelating agent were checked for the presence of copper by flameless atomic absorption. The responses of chelating agents for copper are given in table 1. As may be seen from table 1 DEDC contains the minimum copper. Three ligands DEADC, dithizone and acetyl acetone were selected for the chelation and extraction of copper and the existance of copper was checked both in the aqueous and organic phase. The Britton-Robinson buffers were also checked at different pH values for copper impurities. The copper signals by flamess a.a. increases with increasing pH, suggesting that the major source of copper impurities is sodium hydroxide and the idea of using buffer was abandoned. Deionized and triply distilled water were also checked for copper impurities and deionized water was chosen for the study of copper, because it was found to contain no copper.

Total copper was determined by flame (using concentration and absorption mode) and flameless method and was found to be 151.7 ug dm^{-3} and 162.8 ug dm^{-3} with a standard deviation of 0.345 and 4.02 respectively. Free copper was determined by flameless a.a. in the organic phase after chelation with NaDEDC and extraction with MIBK, and injecting 20ul of the organic phase into the furnace. The amount of free copper was then estimated from the prepared calibration plot, and the average value being 4.42ug dm^{-3} with the standard deviation of 0.258. Total copper was also determined by d.p.a.s.v. Avoltammogram of copper in the sampel is shown in fig.1 and table 2 gives a comparison of copper determined using the different analytical techniques.

Identification and determination of chromium and organic contents of "Chromium Spill"

First the optimum parameters for the chelation and extraction of Cr(111) and Cr (vi) were investigated. The optimum pH for chelation of Cr(iv) with APDC and extraction with MIBK was found to be 3-4. The effect of pH on the extraction of Cr(vi) after chelation with APDC is shown in fig.2. The interefenc effect of Cr(111) on

Table-2: The amout of copper in the water sample as determined using different techniques

Techniques	total copper ug dm^{-3}	Standard deviation	Free copper ug dm^{-3}
Flamess atomic absorption spectrophotometry	162.8	4.02	4.42
Flame atomic absorption spectrophotometry	151.7	7.53	
d.p.a.s.v.	162.0	0.345	

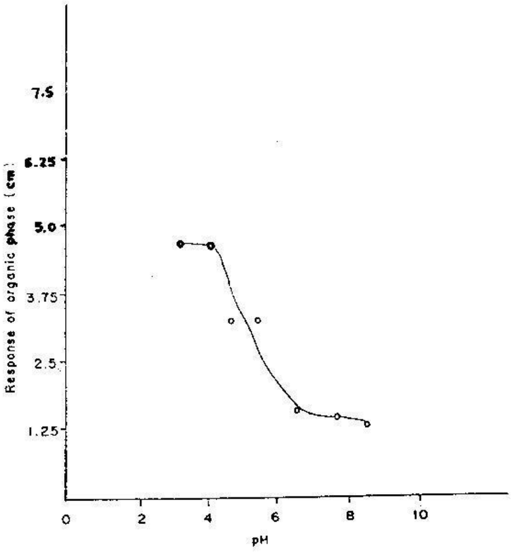


Fig.2: The effect of pH on the extraction of Cr(VI) after chelation with APDC.

the complexation of Cr(vi) at pH 3 was checked. Cr(111) at this pH does not interfere with the chelation of Cr(vi) with ADPC. Similarly for the chelation of Cr(111) with 8 hydroxyquinoline and extraction with MIBK the optimum pH was found to be in the range of 6-8. The intereferences of Cr(vi) on the extraction of Cr(111) after chelation with 8 hydroxquinolin was checked at pH 6, Cr(vi) does not intefere with the extraction of Cr (111).

The amount of total Cr was determined by flame and flameless method. The amount of Cr found by flame method using the concentration and absorption mode is 135 mg md^{-1} and 150 mg dm^{-3} respectively. The average content of total Cr in the sample using flameless method was found to be 133 mg dm^{-3} with a standard deviation of 1.89. For the determination of Cr(vi) in the sample, the sample was chelated with APDC at optimum pH and extracted with MIBK. The organic phase was checked for Cr(iv), but none was found in the sample. This is probably due to the reduction of Cr(vi) by 2 methyl, 1-napthaline by the following reaction and as a result we get Cr(111) and 2 methyl, 1,4,napthaquinone.

For the determination of total Cr in the form of Cr(vi) by D.P. voltammetry, working standard of Cr(vi) were prepared and their d.p. voltammograms recorded. A current voltage plot was prepared. In the same way d.p. voltammograms were recorded for the sample. From the current voltage plot, the amount of Cr in the unknown sample was calculated and is 135 mg dm^{-3}.

Table-3 shows the comparison of total chromium found by different

Table-3: Comparison of different analytical techniques for the determination of chromium in the "Chromium Spill" sample

Techniques	Total chromium found mg dm^{-3}	Cr(III) mg dm^{-3}
Flame atomic absorption absorption mode	140	140
Flame atomic absorption, concentration mode	135	135
Flameless atomic absorption	133	133
D.p.p.	135	135

analytical techniques. There is a very good agrement between the results obtained for both total chromium and Cr(III) by the different analytical techniques employed.

Determination of quinones in Chromium Spill" by d.p.p.

For the determination of quinones n the "chromium spill" sample a standard 10^{-4}M solution of 2 methyl-1,4-napthaquinone was prepared subsequent to information leaked on the nature of the spill. The effect of pH on the d.p. polarographic behaviour of the solution was studied. The reduction current produced was plotted versus pH and the optimum pH obtained.

The optimum pH for determination of 2 methyl-1,4-napthaquinone determined by this method is 8.6 (Britton-Robinson buffer). At pH 8.6, 2-methyl-1, 4-napthaquinone gives a peak at -0.325V. Working standards of 2-methyl-1, 4-napthaquinones were prepared. The reduction current was plotted versus concentration. In the same way a known amount of the "chromium spill" sample was diluted with pH 8.6 buffer, and the reduction current was meausred. Using the calibration plot the amout of 2-methyl-1, 4-napthaquinone in the "chromium spill" sample was calculated and found to be 5.4×10^{-4}M.

Analytical application

The purpose of this study was (a) to investigate the application of anlaytical techniques such as d.p.p., d.p. a.s.v., flame and flameless atomic absorption spectrometry, for the determination of copper and chromium in samples of the aqueous environment in Cork and (b) to make a brief investigation of the speciation of these elements as they exist in the samples. Tables 2 and 3 show that there is a very good agreement between the results of these techniques. The low value of free copper (Cu(II)) as determined by flameless atomic absorption spectrophotometry show that all the copper in the sample is bound copper, but from the result of d.p.a.s.v., it is clear that all the copper is in a labile complexed form being complexed only with inorganic ligands like carbonate and bicarbonate. If copper was bound to organic ligands, then the amount of copper found by d.p.a.s.v. would be noticeably lower than the amount of total copper found by flame and flameless atomic absorption. The study in the second-half of the paper, i.e. the "chromium spill" studies, show that Cr(VI) could be differentiated from Cr(III) using chelation of Cr(VI) with APDC, followed by the determination of the extracted complex by atomic absorption spectrophotometry. Similarly Cr(III) can be differentiated from Cr(VI) by finding out the amount of Cr(VI) by the extraction procedure and substracting this from the total chromium value determined by the atomic absorption method. The difference gives the concentration of Cr(III).

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