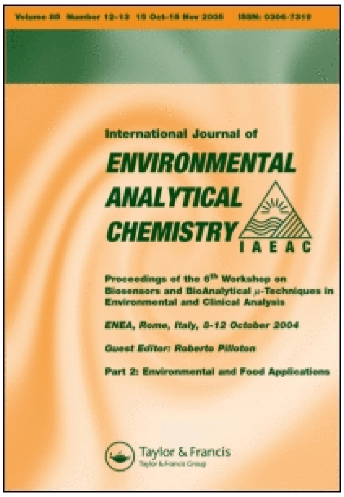

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A SIMPLE ANALYTICAL METHOD FOR MONITORING THE TOTAL CONCENTRATION OF HEAVY METAL IONS IN ENVIRONMENTAL WATERS

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A non-sophisticated analytical procedure has been developed for monitoring the sum of heavy metal elements which form stronger EDTA complexes than manganese(II). It is based on complexation of the heavy metals with EDTA and a catalytic indication of its stoichiometry. The equivalence point is determined visually using the substitution reaction between Mn(II)-EDTA and heavy metal ions, followed by the Mn(II)-catalyzed oxidation of Acid Blue 45 dye with hydrogen peroxide. The method has a reasonable accuracy, uses simple test equipment and stable reagents, there are few interferences and it can be carried out by non-technical personnel. Neither preconcentration nor dilution of the sample is required and it is applicable to aqueous samples containing heavy metals down to ppm levels. Some applications to river and groundwaters are shown.

KEY WORDS: Total heavy metal, environmental water analysis, river water, groundwater, catalytic indication.

INTRODUCTION

The pollution of the aquatic environment due to heavy metal element contamination has become of global concern in recent years. The maximum allowable concentrations of individual heavy metals in tap and natural waters are recommended internationally. Although the determination of selected heavy metal elements is easily done by suitable analytical techniques, e.g. atomic absorption spectrometry, ICP emission spectrometry, X-ray fluorescence spectrometry and anodic stripping voltammetry,[1] few quantitative methods exist which allow the determination of ppm level of total heavy metals without sacrificing precision. There is an urgent need for every laboratory to have inexpensive analytical procedures suitable for use in the field and for routine purposes. The idea of measuring the sum of the heavy metals by spectrophotometry was reported with dithizone[2] and PAR[3] as reagents. The concept, however, has not found widespread application because of the tedious absorbance measurements. A major drawback of spectrophotometry is that absorption maxima of individual metal chelates are not identical and their molar absorptivities differ considerably, which makes the evaluation procedure rather complicated. A PAN gel column method[4] has also been investigated; the length of the coloured band is a measure of total heavy metal ions, but transition metal ions such as nickel and manganese do not give a clear colour reaction.

We have developed a non-sophisticated semiquantitative procedure based on the catalytic indication of stoichiometry. Of the methodology available, complexation of heavy metal ions with EDTA is probably the most effective and convenient. As heavy metal elements form stronger EDTA complex than manganese(II), the release of manganese(II) ion from Mn(II)-EDTA is followed visually by the Mn(II)-catalyzed oxidation of an anthraquinone dye. Among the various indicator substrates investigated, Acid Blue 45 (1,5-dihydroxy-4,8-diaminoanthraquinone-2,6-disulfonate, Na salt; Colour Index 63010) is best suited for the present purpose. This dye has been applied to the catalytic-photometric titration of micromolar amounts of manganese, cobalt, nickel, copper, zinc and cadmium.[5]

EXPERIMENTAL

Reagents and Water Samples

Analytical reagent grade chemicals except Acid Blue 45 were used in the preparation of all solutions. Standard EDTA solution (0.01 M) was prepared from the disodium salt (Dojin, Japan) by weighing and standardized by complexometric titration. Acid Blue 45 (Solway Blue BN, ICI Ltd.) was purified as described.[6]

Collection of surface waters was done under dry-weather flow conditions and all samples were preserved in polyethylene bottles.

Recommended Procedures

Pretreatment of samples According to the monitoring purposes, water samples were pretreated as follows. Procedure I (total of dissolved heavy metals): pass the water sample through a 0.45 μm membrane filter and acidify the filtrate to pH 2 with hydrochloric acid. Procedure II (total of free and bound heavy metals): add 10 ml of 65% nitric acid to the water sample (10 ml) and evaporate it to dryness. Repeat the procedure three times, dissolve the residue in a minimum amount of dilute hydrochloric acid and then dilute to 10 ml with water.

Determination of total heavy metal ions In each of four test tubes, place a 1 ml aliquot of the water sample, 0.1 ml of 10^{-n} M standard EDTA (n = 2,3,4 or 5), 0.08 g potassium hydrogen carbonate, 0.1 ml of 10^{-3} M Mn(II)-EDTA, 0.2 ml of 0.02% Acid Blue 45 and 0.4 ml water in the order given. Mix well and start the catalytic reaction by addition of 0.2 ml of 0.6% hydrogen peroxide. Observe the colour change within 30 sec. For the elimination of calcium interferences, if necessary, add 0.1 ml of 0.2 M sodium fluoride before analysis.

For substoichiometric amounts of EDTA, the Mn(II)-catalyzed oxidation of Acid Blue 45 with hydrogen peroxide proceeds instantaneously and the solution turns from blue to colourless. No colour change is observed when EDTA is in excess in the test solution. Thus the approximate concentration level of total heavy metal ions can be determined visually. Successive treatment of the water sample with an appropriate EDTA solution (e.g. 0.1, 0.3, 0.5 and 0.7 ml of 10^{-n} M

Table 1 Analytical results for synthetic samples

Heavy metals	*Total heavy metal concentration (10^{-4} M)*	
	taken	*found*
Fe	1.3	1.5±0.5
	3.8	5±1
	0.75	0.5±0.1
Fe-Al	1.4	1.5±0.5
Co-Zn-Cd	0.53	0.3±0.1
	2.7	3±1
	5.3	5±1
Co-Ni-Cu	9.7	9±1
Fe-Co-Zn-Cd	1.9	1.5±0.5
	4.6	3±1
	6.3	5±1
	9.1	9±1

standard EDTA; *n* corresponds to the value obtained in the first stage) suffice for the estimation of the total heavy metal content. An accurate result will be obtained within a usable range of standard EDTA solutions.

RESULTS AND DISCUSSION

Selection of Optimum Conditions

Fundamental parameters for the catalytic indication reaction have thoroughly been studied earlier.[6,7] Briefly, the optimum conditions for the Mn(II)-catalyzed reaction are limited to relatively high hydrogen carbonate concentrations and a narrow pH range; a 0.4 M hydrogen carbonate solution (pH 8.4) was chosen as reaction medium. Potassium hydrogen carbonate is preferred because the sodium salt is less soluble. The high hydrogen carbonate concentration contributed to the control of the pH variation in the test samples. Thus no pH adjustment is required for most water sample analyses. The rate of anthraquinone dye oxidation is zero order with respect to the dye concentration. Acid Blue 25 (Colour Index 62055) can be used as an alternative for Acid Blue 45. Metallochromic indicators used for complexometric determinations of heavy metal ions have some critical deficiencies; other metal ions often interfere in the equivalence point detection by blocking the indicators. This problem has been overcome by the catalytic indication method which offers a high colour contrast, i.e. from blue to colourless. The empirical limit of detection is about 10^{-6} M of total heavy metal ions, which is quite sufficient for routine analysis of polluted environmental waters. Analytical results for synthetic samples are shown in Table 1.

In natural waters, trace heavy metal elements may be present in one of the following forms; free ion, inorganic and/or organic complexes, and associated with colloid and particulates.[8,9] To obtain the sum of these species, pretreatment of the water sample is necessary. Heavy metals such as iron and copper are reported to

Table 2 Effect of sample pretreatment on the analysis of total heavy metals

Samples			*Total heavy metals* (10^{-4} *M*)[a]	
			I	*II*
River water	A	(pH 3.3)	1.5±0.5	1.5±0.5
	B	(pH 2.2)	30±10	30±10
	C	(pH 4.0)	1.5±0.5	1.5±0.5
	D	(pH 6.1)	0.5±0.1	0.5±0.1
Groundwater	E		1.5±0.5	1.5±0.5
	F		3.0±1.0	3.0±1.0
	G		0.45±0.05	0.45±0.05

[a] I, samples filtered according to procedure I; II, samples digested according to procedure II.

exist as humic complexes in river water.[10,11] Humic and fulvic acids, however, form much weaker complexes than EDTA. Thus these metal complexes do not interfere and can be determined as a sum of EDTA-reactive heavy metals. Colloidal materials will dissolve when the sample is acidified. According to Florence and Batley,[12] most colloidal particles are included in the dissolved fraction. Filtered and unfiltered river water samples showed no differences in the contents of total heavy metals, as shown in Table 2. Digestion of samples with hot nitric acid (procedure II) was effective for the decomposition of organic sequestering substances present in natural water. This simple pretreatment prevents the risk of underestimation; the fractions bound to organic ligands are now determined.

An EDTA-impregnated reagent strip method is a useful alternative. Ten μl of standard EDTA (normally 3×10^{-n} M) was added to a filter paper (Toyo Roshi No. 51B, 10 × 15 mm) and air-dried. From the number of strips required to retard the catalytic indication reaction, the total heavy metal ion concentration in the sample was determined. The analytical data on river water samples are in good agreement with those of the solution method (see Application section). CyDTA is a much stronger complexing agent than EDTA but it cannot be used because of a slow reaction between CyDTA and heavy metal ions.

Interference Study

Calcium is the predominant cation in most natural waters with concentrations ranging from 10^{-4} to 10^{-2} M. Most of the river waters in Japan have a moderate calcium concentration (average, 2.2×10^{-4} M) and a Ca:Mg ratio of 2.8. The stability constants of the EDTA complexes of manganese(II), calcium and magnesium are $10^{14.0}$, $10^{10.6}$ and $10^{8.7}$, respectively.[13] The low but significant complex-forming ability of calcium enables it to compete with manganese(II) which is liberated in the course of the substitution reaction between Mn(II)-EDTA and heavy metal ions. As it is difficult to estimate the conditional stability constants of Mn(II)-EDTA and Ca(II)-EDTA complexes at high hydrogen carbonate concentrations (0.4 M, pH 8.4), the validity of the method has been evaluated experimentally. Zinc(II) was selected to represent the heavy metal ions; the results

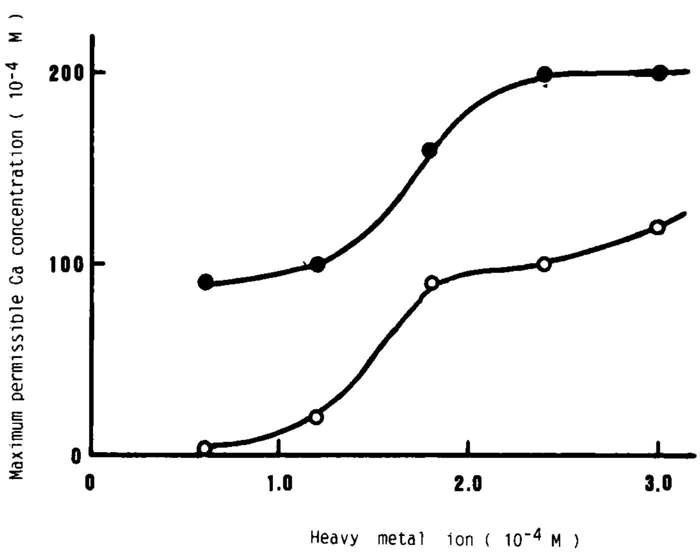

Figure 1 Maximum permissible concentration of calcium for heavy metal analysis. ○, in the absence of NaF; ● in the presence of 0.01 M NaF.

are shown in Figure 1. Calcium poses no interference problems up to at least a 10:1 molar ratio to heavy metals. Serious interferences caused by a large excess of calcium were effectively masked by the addition of sodium fluoride; no filtration of calcium fluoride is necessary before visual detection. Effective removal of calcium was also achieved by its precipitation as oxalate. Calcium carbonate, in a suspended state, did not react with EDTA; the contribution of dissolved calcium salts to heavy metal contents was about 1% from 10^{-3} M calcium. Because of the non-complexing characteristics of suspended silica, no differences were observed in measurements done with and without silica up to 10^{-3} M.

The method can be applied to both laboratory and industrial waste waters. Strong organic sequestering reagents such as EDTA are effectively decomposed by procedure II.[14] There are no problems with the determination and the recovery is satisfactory (cf. Table 3).

Applications

Analysis of polluted river water Samples were taken at several sites on the river Matsukawa, a tributary of the river Mogamigawa (North Japan). It originates from Mt. Azuma (green tuff region) and flows through the Yonezawa basin and into the Japan Sea. An abandoned sulphur mine upstream (altitude, 1350 m) delivers acid water and may have a detrimental effect on the quality of the river water. We are routinely monitoring the water for trace heavy metal pollutants. The total heavy metal ion concentration levels in the river water from 10 locations are presented in Table 4. The first three samples were taken upstream near the closed mine. Extremely high concentrations of total heavy metals at Ainosawa and Shintomasu are mainly due to iron and aluminium, which are dissolved from the

Table 3 Analytical results for synthetic samples containing an organic sequestering ligand[a]

Heavy metals	*Total heavy metal concentration (10^{-4} M)*	
	taken	*found*
Fe	3.8	5±1
Fe-Al	1.4	1.5±0.5
Co-Ni-Cu	9.7	9±1
Fe-Co-Zn-Cd	9.1	9±1

[a] Samples containing 10^{-3} M EDTA were digested according to procedure II.

Table 4 Determination of total heavy metal ions in the river Matsukawa, North Japan

Sampling sites	*Distance from inlet point (km)*	*pH*	*Total heavy metal ion concentration (10^{-4} M)*[a]	
			October 1985	*October 1986*
1. Sanseiko		3.3	1.5±0.5	0.8±0.2 (0.59), 2±1*
2. Ainosawa	0.7	2.3	30±10	20±10 (23), 20±10*
3. Shintomasu	1.8	2.3	15±10	20±10 (22), 20±10*
4. Yazawa	4.5	4.2	3±1	2±1, 4.5±1.5*
5. Goryuten	5.4	4.6	1.5±0.5	2±1, 2±1*
6. Odairabashi	7.5	4.6	1.5±0.5	2±1, 2±1*
7. Ishikido	8.6	4.6	1.5±0.5	0.4±0.1, 0.45±0.15*
8. Fukudabashi	14.0	4.5	0.7±0.1	0.4±0.1, 0.45±0.15*
9. Yagibashi	18.1	6.4	0.1±0.05	<0.1, <0.1*
10. Niidabashi	19.3	6.3	0.3±0.1	<0.1, <0.1*

[a] Asterisks denote values obtained by filter paper method; iron content determined by AAS shown in parentheses.

waste ore residues disposed near the old mine. The hazardous-waste dump has been operated until 1961 and vast quantities of waste were buried near the upstream sites. Clearly, the mining activities have elevated the soluble heavy metal and hydrogen ion concentration. For environmental improvement, a diversion has been made by leading the acid drainage water via a ditch to a number of drilling wells (depth, 100 m). The downstream reduction of the total heavy metal content is obvious. Similar distribution profiles were obtained in 1985 and 1986. The analytical results for acid water samples (Sanseiko, Ainosawa and Shintomasu) were in good agreement with those determined by atomic absorption spectrometry.

The ability to perform panoramic analyses at low concentration levels is important when checking for unexpected pollutants or identifying causes of a pollution accident. A typical example is the accidental contamination of the river Matsukawa at Yonezawa basin. We found a sudden increase of the heavy metal concentration on January 29, 1986. The cause of pollution was identified as the run-off of a copper salt solution from an electronic factory.

Analysis of groundwaters The method has been applied to groundwaters collected from deep aquifers. Sampling was done on the same day in the city of Yonezawa, at depths from 50 to 150 m. The concentration of total heavy metals in the samples ranged from less than 10^{-6} to $(3 \pm 1) \times 10^{-4}$ M. That is, the concentration levels in groundwaters normally were below the detection limit of the method. These estimates have been substantiated by atomic absorption spectrometry, which revealed high levels of naturally occurring iron in five samples and of manganese in three samples. The highest concentration of iron was 2.4×10^{-4} M (13.4 ppm), and that of manganese was 7.7×10^{-5} M (4.2 ppm). The heavy metal composition of groundwaters depends, among other factors, on the geological formation below the water table. Manganese is undoubtedly one of the most ubiquitous metals in the lithosphere, being present in large concentration in a wide range of geological material. Abnormally high concentrations of manganese at selected local aquifers sustain the dissolution equilibrium of surrounding geomatrics in groundwater.

CONCLUSION

The release of heavy metals to the environment, in particular to surface water, necessitates the development of a simple analytical method for their determination. The proposed non-sophisticated procedures are useful to estimate the level of total heavy metal ions. The method works over a wide pH range in samples containing a variety of heavy metal pollutants. In practice the determination of the total amount of EDTA-reactive heavy metal ions is sufficient. The uptake of metals by biological systems is known in most cases to proceed from the free ion state rather than directly from complexes.[15] That is, the sum of soluble heavy metal ions (i.e. free plus labile complexed) is a valuable index for water quality. For characterizing environmental water better, speciation studies are necessary for the subset of relevant samples. The present strategy will help to reduce the total cost of environmental control and of water quality assessment studies.

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