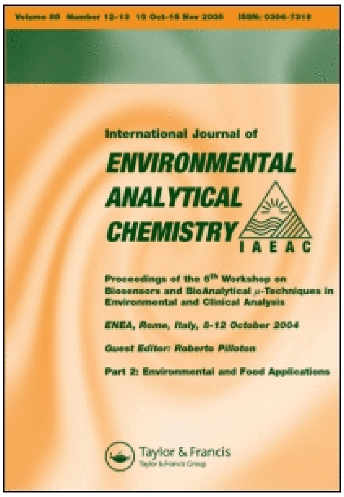

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Synergistic Spectrophotometric and Atomic Absorption Spectrometric Analysis of Zinc in Alloys and Environmental Samples with N-p-MEthoxyphenyl-2-Furylacrylohydroxamic Acid and Pyridylazo Reagents

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SYNERGISTIC SPECTROPHOTOMETRIC AND ATOMIC ABSORPTION SPECTROMETRIC ANALYSIS OF ZINC IN ALLOYS AND ENVIRONMENTAL SAMPLES WITH N-p-METHOXYPHENYL-2-FURYLACRYLOHYDROXAMIC ACID AND PYRIDYLAZO REAGENTS

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Zinc (II) was selectively extracted from aqueous solutions of pH 7.8–8.5 into chloroform with N-p-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA). 1-(2-pyridylazo)-2-naphthol (PAN) or 2-[(5-nitro-2-pyridyl)azo]-1-naphthol (NPAN) were added to the extract to form intensely coloured ternary complexes measurable spectrophotometrically at 550 nm ($\varepsilon = 6.03 \times 10^4 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$) and 625 nm ($\varepsilon = 8.15 \times 10^4 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$) respectively. For atomic absorption spectrometric analysis, methyl isobutyl ketone (MIBK) was used as extracting solvent instead of chloroform and the zinc-MFHA-MIBK extract was aspirated directly into an air-acetylene flame. The absorbance was measured at the 213.9 nm resonance line with a detection limit of 0.05 ppb, which was significantly better than the limit of 1.0 ppb achieved for zinc previously with flame AAS. The method tolerated a large number of anions and cations normally occurring with zinc in environmental samples, and was applied to the trace analysis of zinc in alloys, coal, plant tissues, animal tissues and natural waters. The combinations of MFHA and PAN/NPAN were chosen from eleven hydroxamic acids and nine pyridylazo reagents as detailed in the paper.

KEY WORDS: AAS, alloys, environment, spectrophotometry, zinc, hydroxamic acids, pyridylazo reagents.

INTRODUCTION

Zinc in the Environment

Zinc is an ubiquitous element; it is essential as well as toxic depending on the level of exposure and the target species.[1] It is a component of more than twenty metalloenzymes operative in mammals and plays a vital role in the biosynthesis of several life-sustaining chemicals.[2] A number of physiological processes, including healing response of tissues, hormone metabolism, immunisation and stabilisation of ribosomes, require zinc.[3] Beyond the trace levels required for sustaining such

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processes, however, zinc can be toxic and has been the cause of metal-fume fever, pneumonitis and dermatitis in humans.[2] Several species of lower animals and plants, which are a part of the human food-chain, are highly susceptible to zinc, incapable of tolerating it even at levels of the order of 0.007 ppm[1]. The prevailing environmental standard for maximum allowable concentration of zinc in effluent discharged to streams is 1.0 ppm and for the presence of zinc in irrigation water for long-term use is 5.0 ppm.[4] Several recent studies by the author[4-7] have revealed that these levels may be highly toxic to several useful organisms and lower levels need to be recommended in the water quality standards. The wide industrial application of zinc, which has sharply increased in recent years causing the production in the 1970s to be more than double that in the 1950s,[1,8] has also led to increasing release of zinc through gaseous, aqueous and particulate emissions, into the environment.

The Present Method

The omnipresence of zinc in the environment and its dual physiological role makes it necessary to have highly sensitive, selective and rapid methods of analysis for zinc in environmental matrices for use in the monitoring and management of the metal. The present methods fulfil this criteria and enable accurate determination of zinc down to levels lower than 10^{-4} pmm (0.1 ppb). The methods are more sensitive and selective than the prevailing spectrophotometric or flame-AAS methods,[1,9-13] and are based on the selective extraction of zinc from aqueous solutions into chloroform or MIBK with N-p-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA). For spectrophotometric microdetermination, 1-(2-pyridylazo)-2-naphthol (PAN) or 2-[(5-nitro-2-pyridyl)azo]-1-naphthol (NPAN) are added to the Zn-MFHA extract and the resulting ternary complexes are measured at 625 nm. For AAS microdetermination the Zn–MFHA–MIBK extract is directly aspirated into the air–acetylene flame and determined using the 213.9 nm resonance line. The same solvent could not be used for both the instrumental methods because chloroform was not suitable for AAS while the colour of Zn–MFHA–PAN/NPAN systems was significantly less intense in MIBK than in chloroform. MFHA and PAN/NPAN were chosen from amongst eleven hydroxamic acids and nine pyridylazo reagents. The hydroxamic acids (Table 1) were earlier introduced by us[14,15] as the new and the more sensitive and selective analogues of N-phenylbenzohydroxamic acid (PBHA) which is a versative analytical reagent extensively used in analysis for a large number of metal ions.[16,17]

EXPERIMENTAL

Reagents

All chemicals were analytical reagent grade unless otherwise stated. Deionised and double-distilled water was used for all purposes. N-phenyl-2-furylacrylohydroxamic

Table 1 Spectral characteristics of ternary systems involving zinc(II), hydroxamic acids, and PAN or NPAN in chloroform

Hydroxamic acid	*Ternary system with PAN*		*Ternary system with NPAN*	
	λ_{max}, *nm*[a]	ε, $l\,mol^{-1}\,cm^{-1}$[b]	λ_{max}, *nm*[a]	ε, $l\,mol^{-1}\,cm^{-1}$[b]
N-p-Methoxyphenyl-2-furylacrylo-	550	6.03×10^4	625	8.15×10^4
N-m-Methoxyphenyl-2-furylacrylo-	550	5.84×10^4	625	7.95×10^4
N-p-Tolyl-2-furylacrylo-	545	5.72×10^4	620	7.71×10^4
N-m-Tolyl-2-furylacrylo-	545	5.52×10^4	620	7.47×10^4
N-Phenyl-2-furylacrylo-	540	5.25×10^4	615	7.19×10^4
N-p-Chlorophenyl-2-furylacrylo-	530	5.01×10^4	610	6.94×10^4
N-m-Chlorophenyl-2-furylacrylo-	530	4.87×10^4	610	6.71×10^4
N-p-Bromophenyl-2-furylacrylo-	525	4.59×10^4	600	6.25×10^4
N-m-Bromophenyl-2-furylacrylo-	525	4.45×10^4	600	6.18×10^4
N-p-Iodophenyl-2-furylacrylo-	520	4.18×10^4	595	5.83×10^4
N-p-Nitrophenyl-2-furylacrylo-	510	3.74×10^4	585	5.16×10^4

[a] Wavelength of maximum absorbance.

[b] Molar absorbance at λ_{max}.

Table 2 Spectral characteristics of ternary complexes involving zinc(II), N-p-methoxyphenyl-2-furylacrylohydroxamic acid and pyridylazo reagents

Pyridylazo reagent	*Wavelength of maximum absorbance* (λ_{max}), *nm*	*Molar absorptivity at* λ_{max}, $l\,mol^{-1}\,cm^{-1}$
1-(2-Pyridylazo)-2-naphthol [PAN]	550	6.03×10^4
4-(2-Pyridylazo) resorcinol [PAR]	500	5.47×10^4
2-(2-Pyridylazo)-1-naphthol [α-PAN]	590	5.18×10^4
5-Bromo-α-PAN [BPAN]	610	5.78×10^4
5-Nitro-α-PAN [NPAN]	625	8.15×10^4
2-(2-Pyridylazo)-p-cresol [PAC]	585	3.13×10^4
N, N-Dimethyl-p-(2-pyridylazo) aniline [DMPAA]	540	3.45×10^4
5-(Diethylamino)-2-(2-pyridylazo) phenol [DEPAP]	545	3.84×10^4
5-Bromo-DEPAP [BDEPAP]	550	4.06×10^4

acid and its ten analogues (Table 1) were synthesised by coupling phenylhydroxylamine or one of its *meta* or *para* derivatives with the oxychloride of furan-2-acrylic acid prepared from the reaction of this acid with thionyl chloride. The details of the synthesis and purification of the compounds are similar to those reported by Tandon and Bhattacharyya,[18] and are detailed elsewhere.[19] The hydroxamic acids were employed as their 0.2% ($2\,g\,l^{-1}$) solutions in chloroform (for spectrophotometry) or MIBK (for AAS). PAN, NPAN, and other Pyridylazo reagents (Table 2) were employed as 0.1% ($1\,g\,l^{-1}$) solutions in ethanol.

The stock standard solution of zinc (0.05 M) was prepared by dissolving the appropriate amount of zinc sulphate in water, adding a few drops of dilute sulphuric acid to attain a pH of 4.5 and diluting to 250 ml with water. The zinc content was determined titrimetrically.[10] More dilute solutions were prepared as required.

Apparatus

The absorption spectra were recorded on Perkin–Elmer model 402 and Hitachi model 220 spectrophotometers. Spectral measurements at constant wavelengths were made with these and a SF-4 (USSR) spectrophotometer employing matched quartz cells of 10 mm path length unless otherwise stated. The pH measurements were made with Industrial Electronics Corporation model 092 and Elico model PE 132 pH meters. Atomic absorption spectrometric analyses were carried out with Instrumentation Laboratory model 951/551 instruments.

Procedure for Extraction and Determination

A 10 ml volume of the sample containing 10–30 μg of zinc(II) was adjusted to pH 8.0 with disodium tetraborate buffer and 0.1 M ammonia solution, and was transferred to a 100 ml separating funnel. To it 10 ml of 0.2% MFHA solution was added. The contents were shaken for 20 min. The phases were allowed to separate and the colourless organic layer was transferred to a 25 ml calibrated flask, after drying over anhydrous sodium sulphate. To ensure the complete recovery of zinc the extraction was repeated with two 2 ml volumes of reagent solution for 5 min each. A 3 ml volume of 0.1% PAN or NPAN solution was added to the calibrated flask and finally the combined extract was diluted to 25 ml with ethanol. The absorbances of the red Zn–MFHA–PAN complex or the blue Zn–MFHA–NPAN complex were measured at 550 nm or 625 nm respectively against reagent blanks which were prepared similarly but in the absence of zinc. For atomic absorption spectrometric analysis MIBK was used instead of chloroform with MFHA for the extraction of zinc. Other details were same as above except that the extraction time with MIBK was only 5+2 minutes and the extract was made up to 25 ml before AAS determination with MFHA–MIBK reagent solution omitting the addition of PAN or NPAN. The extract was aspirated directly into the air–acetylene flame and measured with the 213.9 nm resonance line from a zinc hallow cathode lamp. The lamp current was set at 15 ma and slit width at 2 nm. Optimal sample uptake rate was 4.0 ml min^{-1}.

RESULTS AND DISCUSSION

Choice of MFHA and PAN/NPAN

N-Phenyl-2-furylacrylohydroxamic acid and its ten analogues (Table 1) were explored for the extraction—determination of zinc(II) in conjunction with nine pyridylazo reagents (Table 2). The zinc-hydroxamic acid extracts in chloroform or MIBK were colourless but on addition of pyridylazo reagents strongly coloured ternary complexes were formed. Of the eleven hydroxamic acids, MFHA proved to be most selective for zinc(II) and the Zn–MFHA extract in chloroform gave the most sensitive colour reaction with the pyridylazo reagents. Table 1 gives the molar absorptivity figures for the Zn–hydroxamic acid–PAN/NPAN ternary systems. Similar trends were observed with other pyridylazo reagents but the molar absorptivities were always lower than with PAN or NPAN, as illustrated with MFHA as the hydroxamic acid in Table 2. The combination of MFHA with PAN/NPAN was therefore chosen to achieve maximum selectivity and sensitivity.

Choice of Extracting Solvents

Chloroform, carbon tetrachloride, benzene, and MIBK were tried as extracting solvents. Zn–MFHA–chloroform extracts were not suitable for aspiration in the AAS flame as the presence of chloroform produced toxic pungent gases ($COCl_2 + HCl$) in the flame. The sensitivities of AAS signals were also higher when MIBK was the solvent, compared to chloroform, carbon tetrachloride or benzene. Similar observations on the disadvantage of using chlorinated solvents and advantages of using MIBK in AAS have been made earlier.[13] On the other hand chloroform was preferred as extracting solvent for spectrophotometric analysis as the ternary complexes attained the most intense colour in this solvent compared to MIBK, carbon tetrachloride, or benzene.

Effect of pH

The effect of pH on the extraction of zinc with MFHA in chloroform or MIBK was studied at the pH range 1.0–10.5. It was observed that the extraction commenced at pH 6.0 and reached a maximum between pH 7.8 and 8.5 (Figure 1). Above pH 8.5 the extraction decreased. Hence pH 8.0 was chosen for all extraction work.

Effect of MFHA Concentration

Different amounts of MFHA (in chloroform of MIBK) were taken for the extraction of zinc. It was found that 10 ml of 0.2% MFHA solutions were sufficient for the complete extraction of the metal (Table 3).

Effect of PAN or NPAN Concentration

Various amounts of the PAN or NPAN solutions in ethanol were added to the colourless Zn–hydroxamic acid complex. It was observed that 3 ml of 0.1% solutions were sufficient for complete colour development.

Effect of Shaking Time, Stability and Recovery

An equilibration time of 20 + 10 min was sufficient for the complete and quantita-

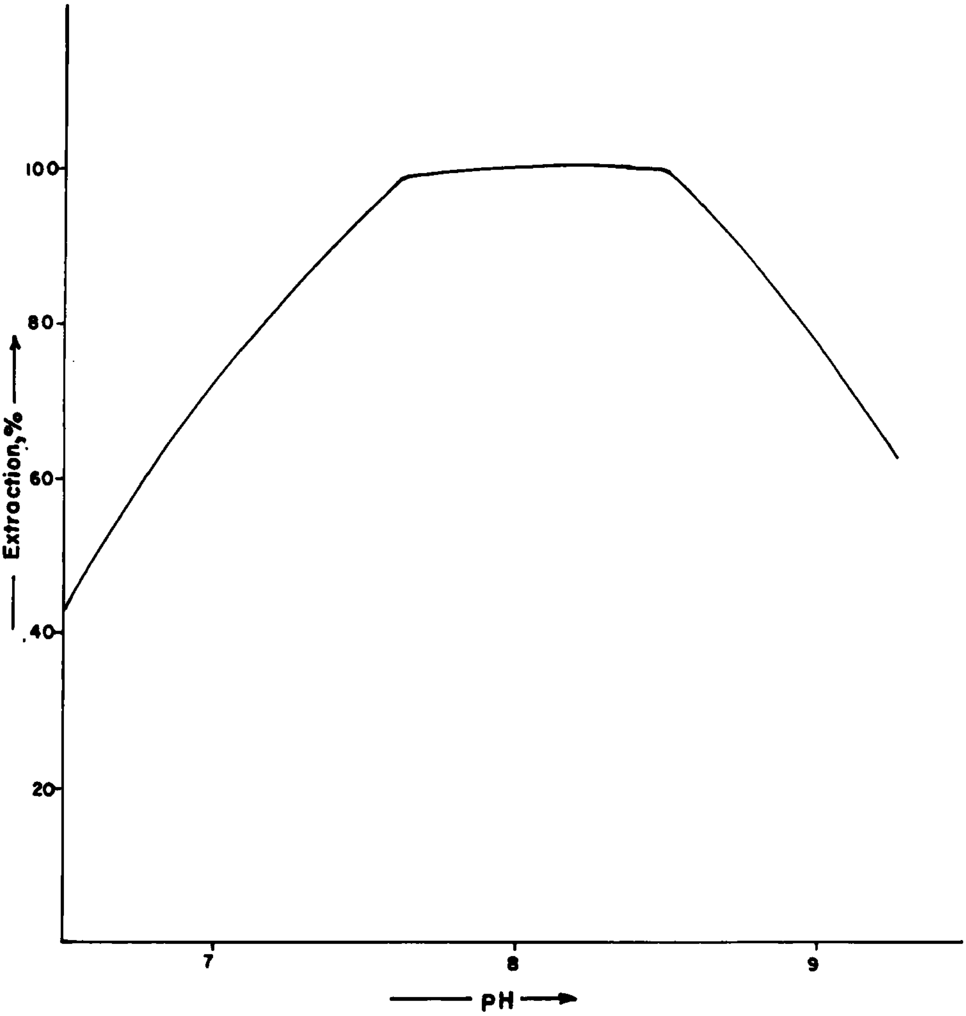

Figure 1 Extraction of zinc(II) with chloroform or MIBK as a function of pH.

Table 3 Effect of MFHA concentration on the extraction of 1 mg l^{-1} of zinc(II) into chloroform/MIBK

Amount of reagent, ml	*Extraction, %*
2.0	30
5.0	40
7.0	75
10.0	100
15.0	100

Table 4 Effect of shaking time on the extraction of $1\,mg\,l^{-1}$ of zinc(II) by $2\,g\,l^{-1}$ MFHA in chloroform or MIBK

Time, min	*Extraction, %*
5	45
10	70
20	100
25	100
30	100

tive extraction of zinc with MFHA in chloroform (Table 4). The complex remained stable for 12h. Likewise the adequate equilibration time when MIBK was used was 5+2min.

Enrichment Studies

Zinc was extracted from various volumes of aqueous solutions ranging from 25 ml to 500 ml, each containing 20 μg zinc, into 25 ml of organic phase and determined. The results indicated that a 15-fold enrichment of zinc is possible with chloroform as well as MIBK extraction without adversely effecting the zinc recovery.

Beer's Law and Sensitivity

The absorption spectra are depicted in Figure 2. The calibration graphs for zinc were obtained under the optimum conditions. Beer's Law was observed over the range 0.4–1.8 ppm of Zn–MFHA–PAN at 550 nm with a molar absorptivity of $6.03 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ and 0.2–1.4 ppm of Zn–MFHA–NPAN system at 625 nm with a molar absorptivity of $8.15 \times 10^4\,l\,mol^{-1}\,cm^{-1}$. The sensitivities of the PAN and NPAN based methods for zinc, as per the definition of Sandell,[20] are 0.001 and 0.0007 ppm respectively. By enrichment and by using 10 cm cells for optical measurements, it is possible to accurately determined zinc levels as low as 10^{-4} ppm (0.1 ppb). The concentration of zinc giving 1% absorption with AAS was 0.05 ppb. This detection limit could also be enhanced 15-fold through enrichment.

Effect of Stripping Agents

Zinc was stripped, after extraction into the organic phase, with 5.0 ml of various stripping agents at different concentrations (Table 5). Stripping was found to be quantitative when the concentration of mineral acid stripping agent exceeded 0.05 M. The best stripping agent was 1.0 M HCl in terms of ease in handling and phase separation.

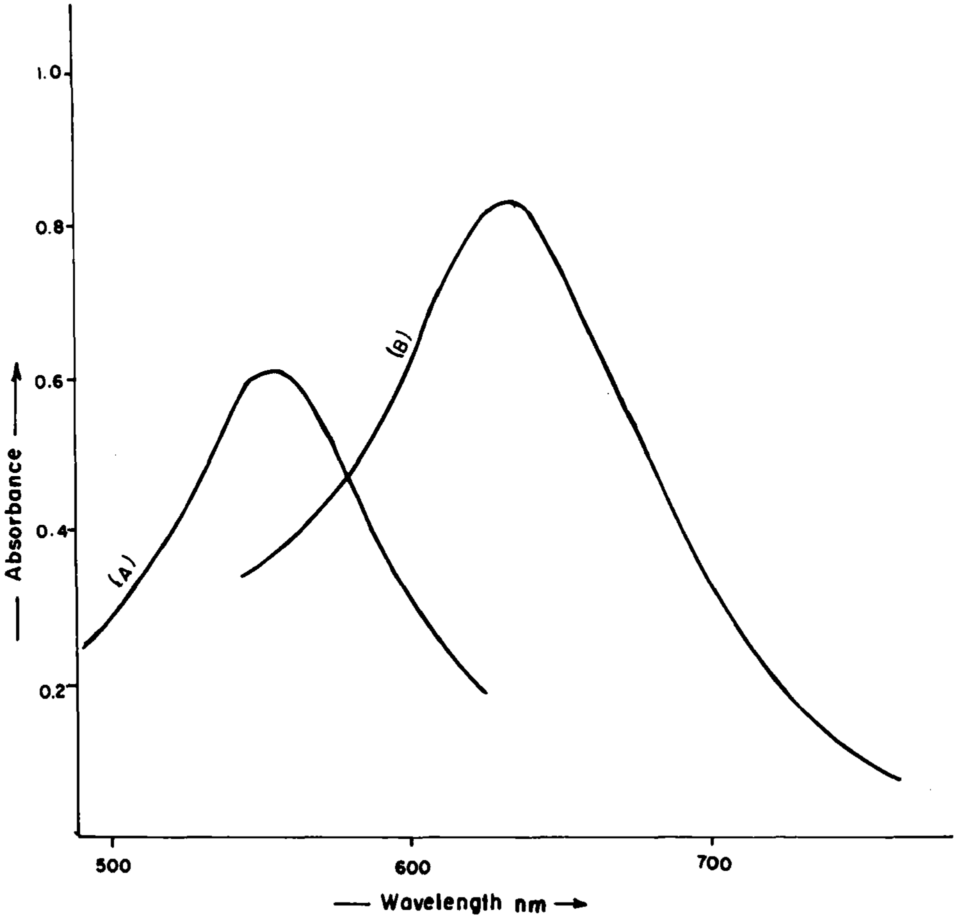

Figure 2 Absorption spectra of (a) Zinc-MFHA-PAN and (b) Zinc-MFHA-NPAN systems in chloroform against reagent blank.

Table 5 Back-extraction of Zn ($1\,\mu g\,ml^{-1}$) from MFHA-chloroform/MIBK extracts by stripping agents

Stripping agent	*Back-extraction, %*				
	0.1 M	*0.5 M*	*1.0 M*	*1.5 M*	*2.0 M*
HCl	45	70	100.0	100	100
H_2SO_4	36	39	44	-	60
$HClO_4$	25	37	51	-	57

Table 6 Effect of diverse ions on the determination of 0.65 µg ml^{-1} of zinc in 25 ml sample

Ion	*Added as*	*Tolerance limit, µg*	
		MFHA-PAN system	*MFHA-NPAN system*
Cations			
Li^+	LiCl	>20000	>20000
Na^+	NaCl	>20000	>20000
K^+	KCl	>20000	>20000
Be^{2+}	$BeCl_2$	20000	20000
As^{3+}	As_2O_3	20000	20000
Ca^{2+}	$CaCl_2$	15000	15000
Ba^{2+}	$BaCl_2$	15000	15000
Sr^{2+}	$SrCl_2$	15000	15000
Ag^+	$AgNO_3$	12000^e	10000^e
Cu^{2+}	$CuSO_4$	12000^c	10000^c
Co^{2+}	$CoSO_4$	10000^g	8000^g
Hg^{2+}	$HgSO_4$	8000^f	7000^f
Pb^{2+}	$Pb(NO_3)_2$	8000	8000
Cd^{2+}	$CdSO_4$	8000^e	7000^e
V^{5+}	NH_4VO_3	6000^a	6000^a
Nb^{5+}	Nb_2O_5	6000^a	5000^a
Fe^{3+}	$Fe_2(SO_4)_3(NG_4)_2SO_4$	6000^b	5000^b
Mo^{6+}	$NH_4Mo_7O_{24}$	5000^b	5000^b
Ti^{4+}	$TiCl_4$	5000^d	5000^d
Anions			
F^-	NaF	>20000	>20000
Cl^-	KCl	>20000	>20000
Br^-	KBr	>20000	>20000
I^-	KI	>20000	>20000
CH_3COO^-	CH_3COONa	>20000	>20000
NO_3^-	KNO_3	20000	20000
ClO_4^-	$KClO_4$	15000	15000

[a] Removed by prior extraction with MFHA–$CHCl_3$ from 4 M HCl media without loss of zinc.

[b] Removed by prior extraction with MFHA–$CHCl_3$ from 0.01 M HCl media without loss of zinc.

[c] Removed by prior extraction with MFHA–$CHCl_3$ at pH 2.5 without loss of zinc.

[d] Masked with NaF.

[e] Masked with KI.

[f] Masked with KBr.

[g] Removed by precipitation as potassium cobaltimitrite prior to the extraction of zinc.

Stoicheiometry of the Zn–MFHA–PAR Complex

The stoicheiometry of the binary Zn–MFHA complex was determined by taking a fixed amount of metal (5 ml of 5×10^{-5} M) and gradually increasing the amount of MFHA (L_1, 8.4×10^{-5} M), keeping the concentration of PAN constant. The slope of the plot of the distribution coefficient of zinc, $\log D_M$, versus $\log [L_1]$ was found to be 2.0 indicating a metal to ligand (L_1) ratio of 1:2.

The stoicheiometry of the ternary Zn–MFHA–PAN complexes was determined by taking a fixed amount of the Zn–MFHA complex (5 ml of 5×10^{-5} M) in

Table 7 Determination of zinc(II) in alloy, coal, biological materials and natural waters. All values are in ppm unless otherwise stated

Sample	*Zinc present (certified value)*	*Zinc added*	*Zinc found*					
			MFHA-PAN		*MFHA-NPAN*		*AAS*	
			Found (average of eight determinations	*Standard deviation*	*Found (average of eight determinations*	*Standard deviation*	*Found (average of eight determinations*	*Standard deviation*
Magnesium alloy (BAM 208)	0.84%	nil	0.837%	0.004	0.834%	0.006	0.841%	0.004
Coal (SRM 1635)	4.7	nil	4.68	0.05	4.66	0.07	4.69	0.06
	–	2.00	6.69	0.07	6.71	0.07	6.73	0.05
Citrus leaves (SRM 1572)	29±3	nil	29.07	0.06	28.98	0.04	28.95	0.08
Tomato leaves (SRM 1573)	62±6	nil	61.5	0.09	61.2	0.08	62.3	0.09
Frog muscle (uncertified)	–	nil	3.17	0.04	3.20	0.07	3.23	0.08
	–	2.00	5.19	0.11	5.24	0.13	5.20	0.10
Lake water	–	nil	0.074	0.004	0.071	0.004	0.073	0.003
	–	0.05	0.122	0.007	0.122	0.006	0.125	0.007
Pond water	–	nil	0.013	0.003	0.011	0.005	0.014	0.001
	–	0.05	0.064	0.005	0.063	0.005	0.064	0.003

chloroform and gradually increasing the amount of PAN $[L_2]$. The slope of the plot of $\log D_M$ versus $\log[L_2]$ was found to be 2.0 indicating metal to PAN ratio of 1:2 and the ternary zinc–MFHA–PAN colour system to be a 1:2:2 metal:MFHA:PAN adduct. Similar results were obtained with NPAN.

Interference Studies

The tolerance of the proposed methods towards anions and cations other than zinc(II) was studied by determining zinc in 25 ml samples containing $0.65\,\mu g\,ml^{-1}$ of the metal in presence of a large number of anions and cations. The tolerance limit was set at the concentration of foreign ion which would cause less than $\pm 2\%$ error in zinc recovery. The results of the tolerance limits of the spectrophotometric methods are presented in Table 6. It may be seen that a large number of anions and cations which commonly occur with zinc in environmental samples are tolerated to a high degree. The MFHA–NPAN reagent combination was marginally less selective than the MFHA–PAN combination though the latter too had adequate selectivity. The tolerance limits of the AAS method were the same as for MFHA–PAN based spectrophotometric method.

DETERMINATION OF ZINC(II) IN ALLOY, COAL, PLANT TISSUES, ANIMAL TISSUES AND NATURAL WATERS

The samples were processed as detailed elsewhere[14,15,21] and were analysed for zinc by spectrophotometry and AAS by the methods described above. The results from replicate analysis of several certified and uncertified samples, with and without standard addition (Table 7) indicate the precision and accuracy of the methods.

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