

Spectrophotometric determination of zinc at trace level in environmental samples

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Summary. Zinc is selectively extracted with N-hydroxy-N,N'-diphenylbenzamidine and spectrophotometrically determined with 4-(2-pyridylazo)resorcinol. The molar absorptivity is $9.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Relative standard deviation is $\pm 1.5\%$.

A new spectrophotometric method for the determination of zinc with 4-(2-pyridylazo)resorcinol (PAR) by prior separation with N-hydroxy-N,N'-diphenylbenzamidine [1] (HDPBA) at trace level has been developed. It is based on the selective extraction of Zn(II) with HDPBA in chloroform at pH 8.5 to 10.3 using carbonate-bicarbonate buffer [2]. The complex has a molar absorptivity of $8.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 410 nm. A $(2.8 - 5.6) \times 10^{-3} \text{ mol/l}$ HDPBA in chloroform was found to be adequate for complete extraction of the complex.

The sensitivity of the method is further increased by addition of PAR at pH 9.0 (± 0.2) in the aqueous phase after stripping Zn(II) with 0.2 mol/l HCl. The reddish coloured complex has a molar absorptivity of $9.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 495 nm. At least $(3.4 - 9.1) \times 10^{-5} \text{ mol/l}$ PAR in methanol is required for full colour development of the complex.

The Zn(II)-HDPBA and Zn(II)-PAR complexes obey Beer's law upto 6.0 μg and 0.8 μg of Zn(II) ml^{-1} , respectively. Chloroform was chosen as solvent due to the more selective separation of Zn(II) than with polar solvents viz. 1-pentanol, 4-methylpentane-2-one or ethyl acetate and the higher colour intensity of the complex than in carbon tetrachloride, xylene, benzene or toluene. A shaking time of 1 min is sufficient for complete extraction of Zn(II). The complexes are stable for at least 8 h at room temperature (25°C). The stoichiometries of Zn(II)-HDPBA and Zn(II)-PAR complexes were determined by the curve-fitting method and were found to be 1:2 in both cases. The Sandell's sensitivity and the detection limit [3] of the method is $6.95 \times 10^{-4} \mu\text{g cm}^{-2}$ and 1.3 $\mu\text{g Zn(II) l}^{-1}$, respectively. The relative standard deviation for 10 replicate measurements was found to be $\pm 1.5\%$.

Procedure

A. Selective extraction of zinc(II) with HDPBA. Take an aliquot of the test solution containing upto 60 μg Zn(II) in a 100-ml separatory funnel. Adjust the pH of the solution to 9.5 (± 0.2) using carbonate-bicarbonate buffer to an ultimate of 10 ml aqueous phase. This solution is equilibrated by shaking with 5 ml chloroform solution of HDPBA for 2 min. Separate and dry the yellow coloured chloroform extract over anhydrous sodium sulphate (2 g) in a 25 ml beaker. Wash the aqueous

phase twice with 2 ml fresh chloroform. Combine all the washings, after drying, together with the chloroform extract and make the volume upto the mark with chloroform in a 10-ml volumetric flask. The absorbance is measured at λ_{max} against reagent blank.

B. Determination of Zinc(II) with PAR. Take an aliquot of test solution containing upto 8.0 μg Zn(II) in a 100 ml separatory funnel and extract with 5 ml chloroform solution of HDPBA as described above. Discard the aqueous phase and back extract the metal into 5 ml of 0.2 mol/l hydrochloric acid solution. Neutralise this solution with borax buffer and adjust the pH to 9.0 (± 0.2). To this add 0.3 ml of 0.1% PAR solution. Make up the solution to 15 ml with water and measure the absorbance at λ_{max} against a reagent blank.

The following diverse ions (amounts in mg are given in parenthesis) do not interfere in the determination of 0.5 μg Zn(II) ml^{-1} : Cd^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} (1.0); Cu^{2+} , Fe^{2+} , Hg^{2+} , Bi^{3+} (1.7); Sb^{3+} , La^{3+} , Al^{3+} (2.0); Mn^{2+} , Se^{4+} , phosphate (2.5); Mg^{2+} , Ca^{2+} , oxalate (3.0); Ba^{2+} , As^{3+} (4.0); tartarate (6.0); citrate, thiourea (8.0); I^- , thiosulphate (10.0). However, Pb(II) and Cd(II) interfered as these are also co-extracted along with zinc. They were masked with 1 ml each of 5% (w/v) sodium thiosulphate and iodide. When Ni(II) and Co(II) are present over a 10-fold molar excess in real samples, the differential demasking technique [4] after addition of cyanide was used, in which the cyanide complexes of the metal present including zinc were formed and zinc was then preferentially demasked with 1.0 ml of 0.2% (v/v) formaldehyde. The Zn(II)-PAR complex formed by the liberated Zn(II) was then determined spectrophotometrically. An at least 200-fold molar excess of Ni(II), Co(II), Pb(II) and Cd(II) can be tolerated.

The method has been successfully applied for the determination of zinc(II) in standard samples, industrial waste water, coal and fly ash (Table 1). It enables the selective as well as

Table 1. Analysis of zinc in environmental samples

Sample	Zn(II) found, in ppm		RSD of the present method %
	Present method	AAS	
USGS ^a – BHVO ^b – 1	8.6	8.5	1.4
G ^b – 2	10.3	10.27	1.5
Total waste water ^b BSP, Bhilai, M. P.	2.3	2.1	1.4
Fly ash, ^b NTPC, Korba, M. P.	8.1	8.0	1.3
Coal ash, ^b NTPC, Korba, M. P.	10.2	10.4	1.5
BNC Mills, Rajnandgaon, M. P.	4.2	4.05	1.4

(n = 5)

^a United States Geological Survey standards. Certified zinc content: BHVO-1 = 85 ppm; G – 2 = 102.6 ppm

^b The original samples were diluted (after treatment) 10-fold with distilled water.

sensitive spectrophotometric determination of Zn(II) as compared to the previously reported method [5–9]. Most of these methods are less sensitive [5–7, 9], tedious and non-selective [6–8] as many of the common ions generally found associated with zinc interfere.

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Spectrophotometric determination of La, Ce, Pr and Nd in the presence of copper by use of arsenazo III

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Summary. Arsenazo III was applied to the determination of the total amount of La, Ce, Pr and Nd in the presence of Cu, using sodium thiosulphate for masking Cu up to 50 mg. The lanthanides can be analyzed within the range of 0–2.4 or in presence of Pb, Al, Ni, Fe 0–1.6 mg/l. Interferences of Zn, Mn, Ni, Al, Sn, Pb and Fe were examined. The procedure was applied to the determination of Ce in CuSnCe alloys and Al and Pb brasses without prior separation of the matrix.

Experimental

Reagents. 0.05% Arsenazo III, 10% sodium thiosulphate, 1 mol/l acetic acid, 5% citric acid aqueous solutions were used. Basic lanthanides solutions (1 mg/ml) were obtained by dissolving "Specpure" oxides (Johnson & Mathey) in conc. nitric acid.

Decomposition of alloys. 0.25 g of alloy was digested in 5 ml of hot HNO₃ (1:1) and heated for 1 h under a watch glass, then evaporated to about 0.5 ml and diluted with water to 10 ml.

In the case of multicomponent alloys a small amount (about 0.2 ml) of conc. hydrochloric acid should be added during the decomposition of the samples followed by twice evaporating the residue with 3 ml of conc. nitric acid.

A precipitate of stannic acid, if any, was filtered off and washed with diluted nitric acid. The filtrate was evaporated to about 0.5 ml and diluted with water to the mark in a 50 ml standard flask. Aliquots of 5 ml were taken for the determination of the lanthanides.

Analytical curve. Suitable amounts of lanthanides, Cu(II) and other matrix components (if necessary) were placed into a small beaker; then 1 ml of acetic acid (procedure a) or citric acid

(procedure b) was added. Next, the pH-value was adjusted to about 3 and 5 ml of thiosulphate solution were added. Finally, after adjusting to pH 3.5, 2 ml of arsenazo III solution were added and the sample was diluted to the mark with water in a 25 ml standard flask. The absorbance was measured at $\lambda = 650$ nm against water within 20 min after sample preparation.

Results and discussion

The applied amount of thiosulphate (5 ml 10% solution) is sufficient for masking up to 50 mg Cu/25 ml, what is proved by the results presented in Table 1. To ensure stability of the measurements, the copper concentration should be at least 15 mg/25 ml. Thiourea, commonly used as masking agent, cannot be applied when the copper concentration exceeds 5 mg/25 ml.

The presence of Zn and Mn causes only a small increase in the absorbance of the blank (0.04 for 30 mg Zn; 0.015 for 6 mg Mn), without influencing the slope of the analytical curves for the lanthanides.

Table 1. Determination of La, Ce, Pr and Nd and their total content in solutions containing various copper concentrations in acetate buffered medium. The results are mean values taken from three independent measurements

Element	Added (μg)	Cu, 0.6 (g/l)		Cu, 2 (g/l)	
		Determined s (μg)	Determined s (μg)	Determined s (μg)	Determined s (μg)
La	20	19.5	1.1	20.4	0.9
	40	38.8	1.3	40.8	1.1
Ce	20	20.8	1.0	19.9	1.1
	40	38.5	1.3	38.5	1.3
Pr	20	18.5	1.0	19.1	1.1
	40	40.5	1.2	41.2	1.4
Nd	20	19.0	1.1	19.2	1.0
	40	38.6	1.4	41.1	1.2
Mixture ^a	20	18.5	1.1	19.4	1.0
	40	39.7	1.3	40.8	1.2

^a Total amount of lanthanides calculated as La content. 100 μg of mixture contains 25 μg of each lanthanide