

Spectrophotometric determination of trace amounts of cadmium with iodide and methyl violet

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A selective spectrophotometric method based on the interaction of an anionic iodo complex of cadmium with methyl violet has been described for the determination of trace amounts of cadmium. The developed method is precise, accurate and has been applied to determination of cadmium at trace levels (25 ppb) in sea water and high purity samples of indium and zinc materials.

The hazardous effects of cadmium are well documented¹⁻³. However, it finds wide use as an antifriction agent, rust proofer, cooling agent in enamel and paints and in plastic manufacture and storage batteries. Hence, it is necessary to determine this element at trace levels.

Many of the spectrophotometric methods reported for the determination of cadmium are tedious⁴ and not selective^{5,6}. Some other methods based on the interaction of tetraiodocadmiate(II) anion^{7,8} and bis-(phenanthroline) cadmium(II) cation^{9,10} with dyestuffs of opposite charge, though sensitive are inadequate for practical analysis due to interference from other elements that are frequently encountered with cadmium.

The present study shows that the interaction of tetraiodocadmiate(II) with methyl violet provides a more sensitive method ($\epsilon = 1.5 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) than those based on reaction with pyronine G⁷ ($\epsilon = 9.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) or rhodamine 6 G⁸ ($\epsilon = 8.9 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). The method has been applied for the determination of cadmium in sea water and high purity zinc and indium metal samples. Interfering ions have been successfully eliminated by suitable conditioning of the solution prior to spectrophotometric determination.

Experimental

A Hitachi 220 microcomputer based spectrophotometer with 10 mm matched quartz cells was used for all the spectral measurements. An ELICO LI-120 digital pH meter was used for pH adjustments. All reagents used were of AR grade unless otherwise stated.

All solutions were prepared with doubly distilled water.

A stock solution containing 500 ppm of cadmium was prepared by dissolving 0.2854 g of $3 \text{ CdSO}_4 \cdot 8 \text{ H}_2\text{O}$ in 250 ml of water. The solution was suitably diluted to obtain a standard solution (5 ppm) of cadmium. A solution of sodium citrate (1 M) adjusted to pH 4.0 with HCl was used as the buffer. A 5% aqueous solution of KI and 0.01% aqueous solution of methyl violet were also prepared.

An aliquot (up to 15 ml) of the sample solution containing not more than 5 μg of cadmium was taken in a 25 ml standard flask and treated with 2.5 ml of the citrate buffer (pH 4.0). Potassium iodide and methyl violet (2.5 ml each) were added to the flask and the volume was made up to 25 ml with distilled water. The absorbance was measured in 10 mm cells at 590 nm against a reagent blank. A calibration graph was plotted for 0-5 μg of cadmium standard solutions by the above procedure.

Analysis of high purity zinc and indium metals

Zinc or indium metal (5.0 g) was dissolved in 20 ml of 1:1 HCl and made up to 100 ml. Suitable aliquots containing cadmium in the range 0-5 μg were taken and a solution of sodium citrate (20%, 2 ml) was added. The pH was adjusted to 4.0 using a pH meter, before transferring into the 25 ml calibrated flask and analysing as above.

Results and discussion

The absorption spectra of Cd-I⁻-methyl violet complex was recorded against the corresponding reagent blank. The ternary complex was found to have λ_{max} at 590 nm.

It was found that the formation of the ternary complex was complete in the pH range 3.0-6.0. Citrate buffer was preferred to phthalate or acetate buffer as its presence removes the interference due to 200-fold excess of Pb²⁺, Sn²⁺ and Sb³⁺. For the determination of 0.1 ppm of cadmium, constant and maximum absorbance required addition of at least 2.0 ml of 5% KI and 2.0 ml of 0.01% methyl violet. Under these optimal conditions, the colour development was instantaneous and remained stable for 24 hr. The order of addition of reagents was not critical.

The calibration graph was linear over the range 0-5 μg of cadmium present in a total volume of 25 ml. The molar absorptivity (ϵ) was found to be $1.5 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$.

Table 1—Analysis of sea water samples

Composition of the sample	Aliquot taken (ml)	Cd added (μg in 25 ml solution)	Absorbance
—	—	2.5	0.135
		5.0	0.280
NaCl (20%)	10	—	0.000
	10	2.5	0.134
	10	5.0	0.273
Sea water	10	—	0.003
Na (1.05%), K (0.04%)	5	2.5	0.140
Mg (3.77%), Ca (1.3%)	10	2.5	0.140
Cl (1.89%)	10	5.0	0.280
Deep sea water	10	—	0.001
Na (3.2%), K (0.64%), Mg (3.67%), Ca (1.3%)	10	2.5	0.140
Cl (1.7%)	10	5.0	0.280
Sea water	10	1.25	0.072
Shangumugam, Tvm	10	2.5	0.142
	10	5.0	0.284
Tap water	10	1.25	0.071
	10	2.5	0.140

Ten replicate determinations of standard solutions containing 2.5 μg of cadmium showed a mean recovery of 100.25% with a relative standard deviation of 2.9%.

The combining ratio of cadmium to methyl violet was found to be 1:2 from molar ratio, continuous variation and slope ratio methods. These methods were unsuccessful when used for the determination of the combining ratio of cadmium to iodide, as no colour development took place when they were present in molar proportions. However, the equilibrium shift method indicated a cadmium to iodide ratio of 1:4.

Interference studies

A study on interfering effects of various ions (200 ppm) on the determination of 0.1 ppm of Cd by the proposed method revealed that Li^+ , Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Pb^{2+} , Sn^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} , Be^{2+} , Ni^{2+} , Co^{2+} , VO_2^+ , Mn^{2+} , Cr^{3+} , Fe^{3+} , Al^{3+} , Sb^{3+} , Ti^{3+} , La^{3+} , Ce^{4+} , Zr^{4+} , Th^{4+} , Te^{4+} , Se^{4+} , Sb^{5+} , AsO_4^{3-} , AsO_3^{3-} , VO_4^{3-} , WO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{B}_4\text{O}_7^{2-}$, F^- , SCN^- , oxalate, tartrate, I^- , Br^- and PO_4^{3-} do not interfere.

The addition of 2 ml of 5% thiourea eliminated interference due to Pd^{2+} and Pt^{4+} , while 5 ml of 5% sodium fluoride removed interference due to MoO_4^{2-} . The interference due to Hg^{2+} was overcome by reduction with 2.5 ml of 2% SnCl_2 and centrifuging the turbid solution prior to addition of reagent solution. The addition of 2 ml of 5% urea removed interference due to nitrite.

Table 2—Analysis of high purity metals

Sample†	Amount of Cd added ($\mu\text{g}/\text{g}$)	Aliquot taken (ml)	Cd found ($\mu\text{g}/\text{g}$)	
			Proposed method	AAS/SS MS*
ZnSO_4	—	10.0	1.6	1.6
	2.5	10.0	4.1	4.1
	2.5	5.0	3.3	3.2
Zn oxide	—	5.0	2.8	2.8
	1.25	5.0	4.0	4.1
Zn granules	—	5.0	5.3	5.4
	2.5	10.0	2.0	2.0
Indium metal	—	10.0	3.3	3.3
	2.5	10.0	2.5	2.5*
	2.5	10.0	5.0	4.99*

†5 g/100 ml

*Spark Source Mass Spectrometry

Analysis of synthetic and real samples

Table 1 presents the results of the analysis of synthetic sample solutions of various forms of sea water after eliminating the interferences as described above. The results clearly show that the method can be used for trace level determination of cadmium in polluted sea water samples.

Since the metal ions commonly associated with cadmium, viz., Zn^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} , Ce^{4+} , In^{3+} and WO_4^{2-} do not interfere, the proposed method can be used for determination of cadmium in real samples like high purity indium metal, zinc granules and zinc salts (Table 2). The results obtained have been compared with those obtained using AAS and spark source mass spectrometry. The data obtained on the samples spiked with known amounts of cadmium are also presented. The results show good agreement between the two methods.

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