BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 956—960 (1969)

Determination of a Small Amount of Iodide by Atomic Absorption Spectrophotometry Using a Cadmium Hollow Cathode Lamp

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(Received June 8, 1968)

A new application of atomic absorption spectrophotometry to the determination of iodide has been proposed. The method is based on solvent extraction into nitrobenzene of the colorless ion-pair formed between tris(1,10-phenanthroline)cadmium(II) and the iodide anion, and the subsequent determination of the cadmium concentration in the extract by atomic absorption in an air-acetylene flame at the 2288 Å cadmium line. The absorbance due to cadmium in the extract shows a linear relationship to the concentration of iodide over the range from 4×10^{-6} to 4×10^{-5} M initially present in the aqueous solution. The optimum conditions for the determination of iodide have been established, and the extraction efficiency and the effect of other anions have also been studied.

Since the resonance lines for most nonmetallic elements occur in the vacuum ultraviolet region, it has been impossible to determine these elements directly by atomic absorption spectrophotometry. Indirect determinations of nonmetals can, however, be readily performed with conventional atomic absorption apparatus. One of these methods is based on the stoichiometric formation of ion-pairs with a cationic metal ion chelate; these ion-pairs can then be isolated and determined by atomic absorption, the results being related quantitatively to the associated nonmetal.

It has been found that iodide anions can be extracted into nitrobenzene if the aqueous solution contains an excess of tris(1,10-phenanthroline)-cadmium(II) cations, and it is possible to determine the iodide by spraying the nitrobenzene solution into the flame of an atomic absorption spectrophotometer, with a cadmium hollow cathode lamp used as the light source. A brief preliminary study of this method has already been reported.[1] The present paper will present a detailed quantitative study undertaken to establish a new application of atomic absorption spectrophotometry. This proposed method for iodide is rapid and accurate, and it is different from the previously known colorimetric methods, which are based on the catalytic action of iodide,[2,3] the starch-iodide reaction,[3] triiodide formation,[3] and red-colored ion-pair formation between the iodide ion and the tris(1,10-phenanthroline)iron(II) chelate cation.[4]

Indirect methods for the determination of nitrate,[5] pentachlorophenol[6] and phthalic acid,[7,8] based on the same principle, have recently been reported.

Experimental

Apparatus. The atomic absorption was measured with a Hitachi Model EPU-2 spectrophotometer and a Hitachi Model 0420 atomic absorption attachment equipped with a cadmium hollow cathode lamp. An air-acetylene flame was burned with a water-cooled 9-cm slot burner. The pH values were measured with a Hitachi-Horiba Model H-5 pH meter. The shaking for extraction was carried out with an Iwaki Model KM shaker equipped with time control. The gamma ray counting of ^{131}I was performed with an Aloka Model PSM 801 γ-ray spectrometer equipped with a $1\ 1/2''\phi\times1''$ NaI(Tl) crystal.

Reagents. All the chemicals used were of an analytical reagent grade.

A phenanthroline-cadmium(II) sulfate solution was prepared by dissolving 1.28 g of cadmium sulfate ($3CdSO_4\cdot8H_2O$) and 3.17 g of 1,10-phenanthroline ($C_{10}H_8N_2\cdot H_2O$) in dilute sulfuric acid and by then diluting the mixture to a volume of 1000 m*l* with water. The resulting solution (pH 3) is 5.0×10^{-3} M in tris-(1,10-phenanthroline)cadmium(II) sulfate. A cadmium solution for continuous variation plots was prepared by

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[5] T. Kumamaru, E. Tao, N. Okamoto and Y. Yamamoto, *ibid.*, **38**, 2204 (1965).

[6] Y. Yamamoto, T. Kumamaru and Y. Hayashi, *Talanta*, **14**, 611 (1967).

[7] T. Kumamaru, Y. Hayashi, N. Okamoto, E. Tao and Y. Yamamoto, *Anal. Chim. Acta*, **35**, 524 (1966).

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the suitable dilution of a cadmium sulfate stock solution (1.0×10^{-2} M) which had been standardized by EDTA titration. A standard stock solution of 1.0×10^{-2} M iodide was prepared from potassium iodide dried at 110°C. The concentration of iodide ions was determined by conventional argentometry. The iodide standard solution for the experiment was prepared by diluting an aliquot of this stock solution with water to give a concentration of 1.0×10^{-4} M. A radioactive iodide solution was also prepared from sodium iodide-^{131}I, which had been obtained from the Japan Radioisotope Association. To make the solution pH 5, a 0.5 M potassium dihydrogenphosphate-disodium hydrogenphosphate solution was employed.

Procedure. Tris(1,10-phenanthroline)cadmium(II) iodide was extracted into nitrobenzene; the organic extract was then aspirated directly into the atomic absorption spectrophotometer.

Five milliliters of the phenanthroline-cadmium(II) sulfate solution (5.0×10^{-3} M), 5 m*l* of a 0.5 M phosphate buffer solution (pH 5), and a measured volume of 15 m*l* or less of the sample solution were placed in a 100-m*l* separatory funnel, and, finally, the aqueous phase volume was adjusted to 25 m*l* with water. After 10 m*l* of nitrobenzene had been poured in, the funnel was shaken for 1 min. The two phases clearly separated within 20 min after the end of the shaking. The organic phase was then dried with 1 g of anhydrous sodium sulfate.

The absorption due to cadmium in the organic phase was then determined with the atomic absorption spectrophotometer against a reagent blank used as a reference, and expressed as the initial concentration of iodide in the aqueous phase, based on stock iodide solution used as standards. The instrument-operating conditions included analysis at the wavelength of 2288 Å, a slit width of 0.4 mm, and a lamp current of 7.5 mA (cadmium lamp). The flow rates of gases for the air-acetylene flame were 8.0 *l*/min of air and 1.6 *l*/min of acetylene. The burner height was adjusted to make the light beam pass 6 mm above the tip of the burner.

Results and Discussion

Atomic Absorption Spectrophotometric Variables. *Lamp Current.* Figure 1 shows the effect of the lamp current in the absorption of cadmium. From five series of results, it can be seen that a low lamp current gives the higher absorbance for the cadmium 2288 Å. However this cadmium hollow cathode lamp could not be used with a current less than 5 mA because of its low light intensity. Therefore, the preferable lamp current was decided to be 7.5 mA.

Air-acetylene Flame. The effects of the variation in the air-acetylene mixture on the absorption were also studied. The results are shown in Fig. 2. For convenience, the gas-flow rates were adjusted so that the burner consumes 8.0 *l*/min of air and 1.6 *l*/min of acetylene in subsequent investigations. Under these flame conditions, it was found that the optimum height for the passage of the light beam from the hollow cathode tube through the reducing flame was 5 to 8 mm above the tip of the burner; higher and lower passage of light gave slightly poorer sensitivities.

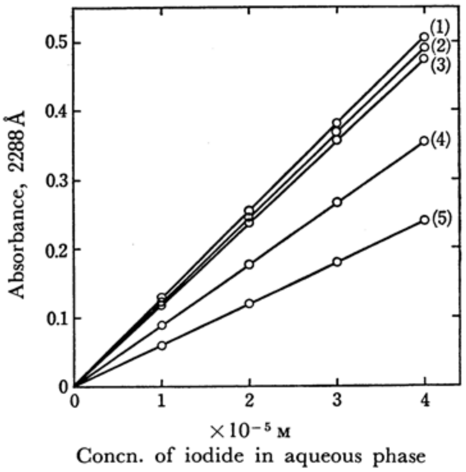

Fig. 1. Calibration curves at various lamp currents.
Lamp current (mA): (1) 5, (2) 7.5, (3) 10, (4) 15, (5) 20
Reference: reagent blank

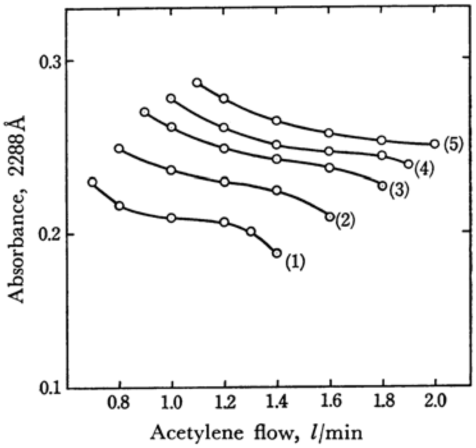

Fig. 2. Effect of variation of air-acetylene mixture on net absorbance for 2.0×10^{-5} M iodide.
Air flow (*l*/min): (1) 6.5, (2) 7.0, (3) 7.5, (4) 8.0, (5) 8.5

Variables of Extraction. *Solvent.* Various kinds of commercially-available organic solvents were tested for the extraction: *n*-butyl alcohol, isoamyl alcohol, isopropyl ether, ethyl acetate, *n*-butyl acetate, methyl isopropyl ketone, methyl isobutyl ketone, chloroform, carbon tetrachloride, 1,2-dichloroethane, cyclohexanone, benzene, chlorobenzene, and nitrobenzene. Only nitrobenzene extracted phenanthroline-cadmium(II) iodide selectively from the aqueous solution. Moreover, nitrobenzene is a suitable solvent for atomic absorption spectrophotometry because it gives a stable flame during the combustion and a higher sensitivity of measurement.

The extraction percentage of iodide was then determined by the radioactive tracer method using an ^{131}I-labeled iodide solution. One milliliter of each phase was taken after extraction, and the radioactivities of gamma rays were measured with a scintillation counter. The results are shown in Table 1. When the phenanthroline-cadmium(II) chelate cations are absent in the aqueous phase, iodide ions were negligibly extracted into nitrobenzene (~200 cpm).

TABLE 1. EXTRACTION PERCENTAGE

Sample No.	Net cpm (^{131}I) Aqueous phase	Net cpm (^{131}I) Organic phase	Extraction percentage, %
1	7475±89	72760±427	90.7±0.7
2	7513±89	72495±426	90.7±0.7

Organic phase: 10 m*l*, Aqueous phase: 25 m*l*
Initial concentration of iodide: 4.0×10^{-5} M
Initial concentration of
tris(phenanthroline)cadmium(II): 1.0×10^{-3} M
pH: 5; buffered with phosphate

pH. The effect of pH on the extraction was studied by extracting the iodide anions from a series of aqueous solutions buffered in the pH range from 2 to 9. In Fig. 3, Curve 2 was obtained by the subtraction of the absorbance in Curve 1 (no iodide) from the total observed absorbance in the sample. The pH variations between 3.5 and 5.5 had practically no effect on the results if the absorbance of the reagent blank was subtracted from the total absorbance at each pH. In the subsequent experiments, the pH of the aqueous phase was adjusted to nearly 5 with a phosphate buffer. The change in the concentration of the phosphate buffer had a negligible effect on the extraction.

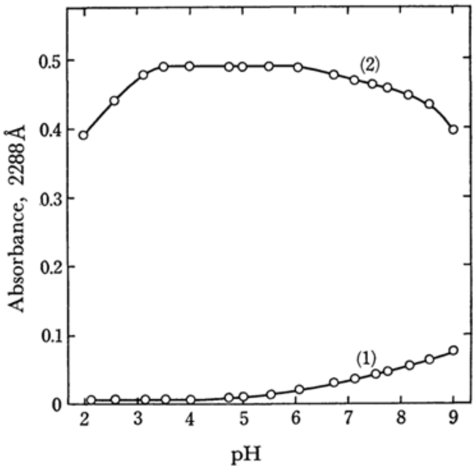

Fig. 3. Effect of pH.
(1) Reagent blank; Absorbance was measured against nitrobenzene.
(2) 4.0×10^{-5} M iodide; Correction in absorbance was made for the reagent blank.

Phenanthroline-Cadmium(II) Sulfate Concentration. As can be seen in Fig. 4, the absorbance of the nitrobenzene phase approached a limit when the chelate concentration was more than 6×10^{-4} M and when the iodide concentration was kept at 4.0×10^{-5} M in the aqueous phase. An excess of at least 15-fold in molar quantity of the phenanthroline chelate to iodide was necessary for quantitative recoveries. Thus the chelate concentration was usually kept at 1.0×10^{-3} M.

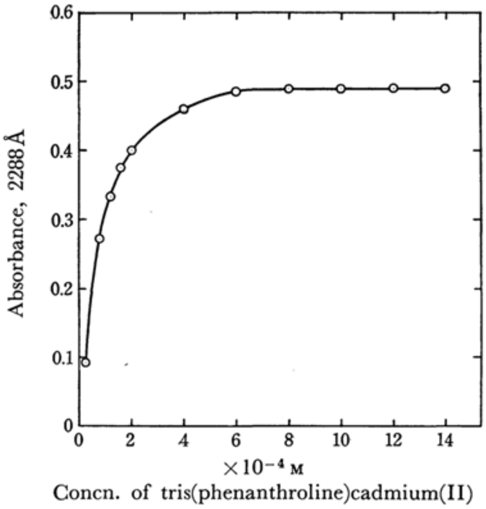

Fig. 4. Effect of chelate concentration on net absorbance for 4.0×10^{-5} M iodide.

Shaking Time. The shaking time for the extraction was varied from 0.5 to 15 min, while the other variables were kept constant. These variations in the shaking time showed that shaking for longer than a 0.5 min did not improve the extraction. Hence, 1 min was employed as the period for the extraction.

Calibration Curve. The standard procedure was decided upon the basis of the above results. The calibration curve was obtained by using varying amounts (1—10 m*l*) of the standard iodide solution (1.0×10^{-4} M). The absorbance due to cadmium in the organic phase showed a linear relationship to the tested concentration range from 4×10^{-6} to 4×10^{-5} M of iodide initially present in the aqueous phase, as is shown in Fig. 1 (Curve 2). This indicates that the high sensitivity of atomic absorption spectrophotometry for cadmium allows the determination of such low concentrations of iodide.

Precision. The reproducibility of the present method was estimated from the results of 10 sample solutions, each 4.0×10^{-5} M in iodide. The average absorbance was 0.490, and the standard deviation was 0.003 absorbance unit (*i.e.* there was a relative error of 0.6%).

Influence of Diverse Ions. The effect of a series of anions on the extraction of the phenanthroline-cadmium(II) iodide into nitrobenzene was examined. Table 2 shows the degree of interference of diverse ions added to the solution containing iodide in 2.0×10^{-5} M.

TABLE 2. EFFECT OF DIVERSE ANIONS ON THE EXTRACTION OF IODIDE

Anion	Added as	[Anion]/[Iodide]	Recovery of iodide, %
F^-	NaF	1000	100
		10000	105
Cl^-	NaCl	1	100
		5	104
Br^-	NaBr	0.1	101
		0.5	106
ClO_3^-	$NaClO_3$	0.01	100
		0.1	108
BrO_3^-	$KBrO_3$	1	100
		10	112
IO_3^-	KIO_3	100	100
		1000	104
ClO_4^-	$KClO_4$	0.01	100
		0.1	111
IO_4^-	KIO_4	0.02	99
		0.1	89
		0.5	110
		1	113
CN^-	KCN	10	102
		100	162
NO_2^-	$NaNO_2$	0.1	100
		1	106
NO_3^-	KNO_3	0.1	101
		0.5	110
CO_3^{2-}	Na_2CO_3	1000	100
$B_4O_7^{2-}$	$Na_2B_4O_7$	1000	100

Concentration of iodide: 2.0×10^{-5} M

It is of interest that the halides, when listed in the order of increasing interference with this method, are fluoride, chloride, and bromide, while the oxyacids and the peroxyacids of the halogens are listed, on the contrary, as iodate, bromate and chlorate, and periodate and perchlorate. One rather strange observation was that periodate appeared to interfere in a negative direction when present in a molar quantity lower than 1/10 the level of iodide. A possible reason for this low recovery may be its oxidation effect on iodide ions. Above this amount of periodate, there appeared an increase in the absorbance with an increase in the periodate; this increase might be caused by interference through the extraction of periodate ions with phenanthroline-cadmium(II). Large amounts of phosphate and sulfate, which were present in the reagent solution used, and carbonate, borate, fluoride, and iodate did not interfere with the determination of iodide, while perchlorate and chlorate, even when 1/10 the molar quantity of iodide was present, gave positive errors.

Composition of Extracted Species. In order to examine the composition of the extracted species, continuous variation plots were made in two series of extraction. As for the determination of the chelate formation ratio of phenanthroline to cadmium(II), the concentration of iodide and the total concentration of cadmium(II) and phenanthroline were both kept constant at 2.0×10^{-4} M, and then the extraction was carried out as in the procedure described above with a series of aqueous solutions containing a varying mole ratio of phenanthroline to cadmium(II). The resulting curve [Fig. 5 (Curve 1)], in which the reagent blank was subtracted, shows the ratio of phenanthroline to cadmium in the extracted species balances at 3; this indicates that the cationic tris(1,10-phenanthroline)cadmium(II) chelate may take part predominantly in the extraction of the iodide ion as the counter ion. Similar plots to confirm the composition of the tris(1,10-phenanthroline)-cadmium(II) iodide are shown in Fig. 5 (Curve 2). This suggests that a 1 : 2 associated ion-pair is formed in the nitrobenzene phase between the tris(1,10-phenanthroline)cadmium(II) cation and the iodide anion; thus the chemical formula of the extracted species can probably be represented as

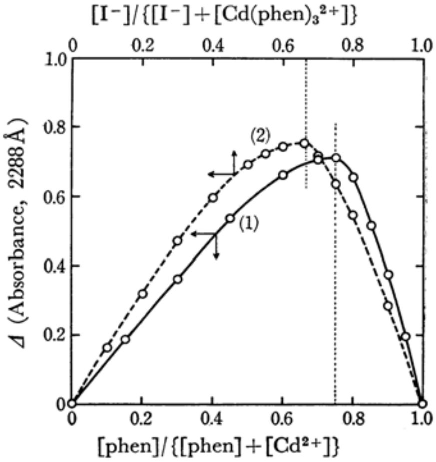

Fig. 5. Continuous variation plots at pH 5.
(1) For phenanthroline-cadmium(II). Total concentration of phenanthroline and cadmium(II): 2.0×10^{-4} M, concentration of iodide: 2.0×10^{-4} M.
(2) For tris(phenanthroline)cadmium(II) iodide. Total concentration of tris(phenanthroline)-cadmium(II) and iodide: 1.6×10^{-4} M.
phen = 1,10-phenanthroline

$[Cd(1,10\text{-phenanthroline})_3] \cdot I_2$.

The author wishes to express his thanks to Professor Yuroku Yamamoto for his kind guidance and encouragement throughout this work, and also wishes to thank Mr. Yuzuru Otani for his technical assistance in this work.