

## Preconcentration of iodide from saline water samples and determination by the catalytic method

K R KRISHNAMOORTHY and R K IYER\*

Analytical Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

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**Abstract.** A method is described for the determination of nanogram levels of iodide in saline water samples. The interfering chloride, present in milligram levels, is eluted out of a column of a strong anion exchanger, retaining the iodide quantitatively. The iodide is then recovered from the column with 2 M ammonium nitrate solution. The determination is carried out by the catalytic method based on the reduction of Ce(IV) by As(III) in presence of iodide. The arresting method was found to be more sensitive. The method can be easily adapted in a field laboratory, with accuracy comparable with neutron activation analysis.

**Keywords.** Iodide; saline waters; preseparation; catalytic method.

### 1. Introduction

Preconcentration of iodide from drinking water and common salt samples followed by its determination by neutron activation analysis was reported by us earlier (Krishnamoorthy and Iyer 1983). The short half-life of I-128 (25 min) necessitates that the laboratory should be situated close to the nuclear reactor. Hence this method cannot be recommended for a field laboratory. The method proposed by Sandell and Kolthoff (1937), based on the catalytic reduction of Ce(IV) by As(III) in presence of iodide, was examined for this purpose. Rodriguez and Purdue (1969) have carried out a detailed study of the factors such as the concentrations of these two reagents, their ratio, temperature and the rate of reaction. Dubravic (1955) arrested the reaction after a fixed time interval by adding Fe(II) solution which reduces the remaining Ce(IV) to Ce(III) producing an equivalent amount of Fe(III). The absorbance of Fe(III)-CNS complex is then correlated with the iodide concentration in the system.

The presence of significant amounts of chloride in natural waters of varying salinity imposed a serious limitation on the application of this method for the determination of iodide (Dubravic 1955; Navada *et al* 1983). This paper describes an anion exchange separation step for eliminating this interference. Further, conditions have been standardized so that the method can be readily adapted in a field laboratory.

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\*To whom all correspondence should be addressed.

## 2. Experimental

### 2.1 Reagents

*Standard iodide solution:* 0.3615 g of AnalaR grade KI was dissolved in deionised water and made up to 200 ml to get a stock solution of 1.382 mg I per ml. This solution is suitably diluted to get the working solution of 100 ng I per ml.

*As(III) solution, 0.2 M:* 9.98 g of arsenious oxide was dissolved in dil NaOH, acidified with H<sub>2</sub>SO<sub>4</sub> and made up to 500 ml.

*Ce(IV) solution, 0.01 M:* 4.043 g ceric ammonium sulphate, tetrahydrate, was dissolved in water containing 90 ml of 1:1 H<sub>2</sub>SO<sub>4</sub> and made up to 1 l.

Ferrous ammonium sulphate solution, 1.5% w/w.

Ammonium thiocyanate solution, 4% w/w.

Sulphuric acid, 1:1.

Ammonium nitrate solution, 0.2 M and 2 M.

Tulsion A-27 (Gel) anion exchanger, -50+100 mesh, in NO<sub>3</sub> form.

All dilutions were carried out with deionised water.

A Shimadzu UV-210A double beam spectrophotometer was used for measuring the absorbance of Ce(IV) at regular intervals and a Beckman model DU spectrophotometer for measuring the absorbance of the Fe(III)-CNS complex.

In order to demonstrate the validity of the experimental conditions, it was necessary to establish the proportionality of the rate constant with the decrease of the concentration of Ce(IV) which follows the first order (Rodriguez and Purdue 1969) and the concentration of iodide which remains unchanged during the reaction (Truesdale and Smith 1975). Expressing mathematically,

$$\begin{aligned} -d[\text{Ce(IV)}]/dt &= k \cdot [\text{Ce(IV)}] \\ &= k' \cdot [\text{Ce(IV)}] \cdot [\text{I}], \end{aligned}$$

where  $k$  is the first-order rate constant and is proportional to the concentration of iodide, i.e.,  $k = k'[\text{I}]$ .

To a series of 10 ml volumetric flasks, containing 0.5 ml of 1:1 H<sub>2</sub>SO<sub>4</sub> and 0.5 ml of As(III) solution, 0 to 80 ng of iodide were added and the volume kept at 8 ml by adding the requisite amount of deionised water. The flasks were kept in a constant temperature bath (a fish pond with an arrangement to keep the flasks in a stable position) for about 15 minutes. Then exactly 0.5 ml of Ce(IV) solution was added to the first flask, simultaneously a stop-watch was started. The flask was made up and the absorbance measured at 360 nm using 1 cm cells, at regular intervals of 2 to 3 minutes. The experiment was repeated for the other flasks. From the plot of log(absorbance) vs. the duration of the reaction, the half-time,  $T$ , for each concentration of iodide was found out. The rate constant  $k$ , given by  $0.693/T$ , is then computed and plotted against iodide concentration. The curve, figure 1, is linear and passes through the origin, in agreement with the equations proposed by Rodriguez and Purdue (1969) and Truesdale and Smith (1975).

This method involves the measurement of Ce(IV) concentration over a period of time and obtaining the rate constant graphically. It would be simpler, especially for routine analysis, to make a measurement of Ce(IV) after a fixed time-interval and

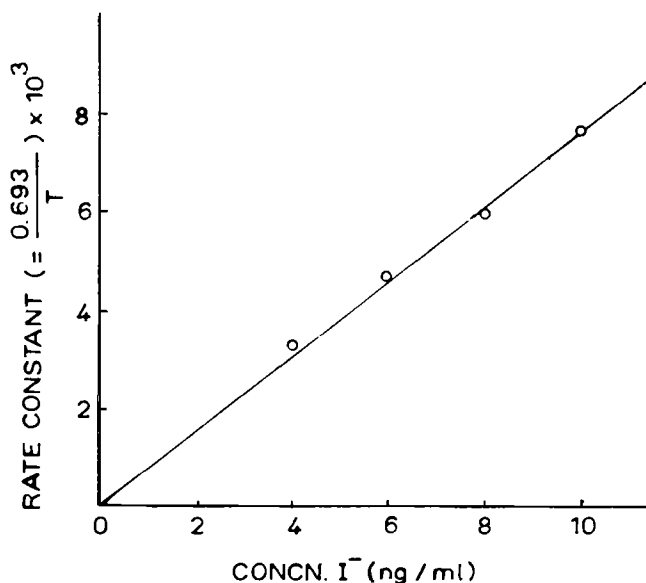


Figure 1. Relation between rate-constant and iodide concentration.

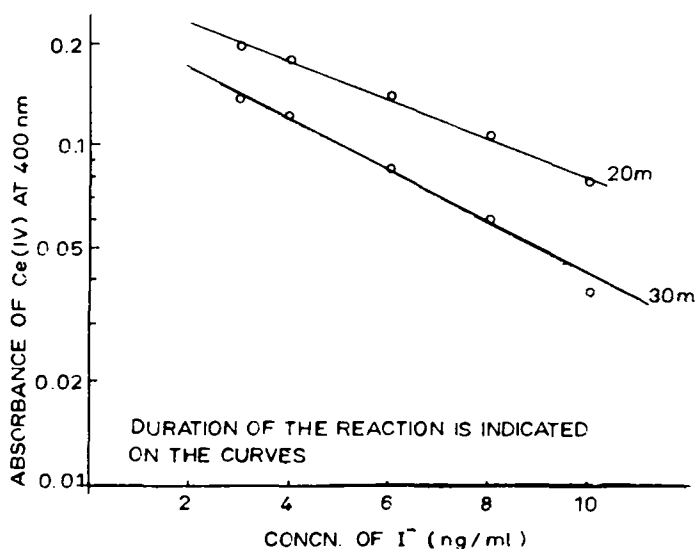


Figure 2. Variation of absorbance of Ce(IV) with iodide concentration.

correlate this with the iodide concentration. This is shown for two intervals of 20 and 30 minutes in figure 2.

A further improvement in this method has been suggested by Dubravic (1955). This is to arrest the reaction after a chosen time interval by addition of excess of Fe(II) solution. This converts the remaining Ce(IV) in the system to an equivalent amount of Fe(III) which can be conveniently estimated by the absorbance of the Fe(III)-thiocyanate complex at 460 nm. We found that this method, in addition to being convenient, is also more sensitive. The time interval is chosen such that the

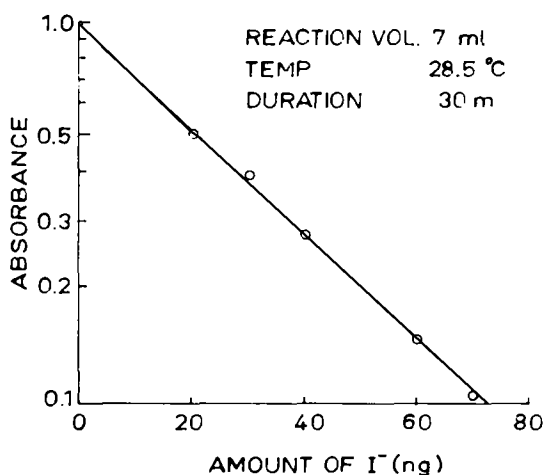


Figure 3. Calibration curve for iodide using the arresting method.

yellow colour of Ce(IV) just fades. This will be smaller when the iodide concentration is higher and vice versa. The feasibility of using this method in the present case was studied by repeating the experiment, keeping the reaction volume at 7 ml. To a series of flasks containing the reagents as before, 0.5 ml of Ce(IV) solution was added at intervals of 0.5 min. At the end of 30 minutes, the reaction was arrested by adding 0.5 ml of Fe(II) solution in the same order at intervals of 0.5 minute. The colour was then developed by the addition of 0.5 ml of thiocyanate solution and the absorbance of the complex measured using 1 cm cells, at 460 nm, after 15 minutes. In this manner, a number of samples could be handled at the same time and analyses carried out conveniently.

Figure 3 gives the calibration curve obtained.

### 3. Preseparation

The presence of chloride in the saline water samples poses a major interference in the analysis by the catalytic method. Thus, the elimination of chloride prior to the determination is required. In our earlier paper, we reported the separation of nanogram amounts of iodide from 1 g of sodium chloride on a column containing 300 mg of Deacidite FF anion exchanger in the NO<sub>3</sub> form. In this step, the chloride content was reduced from 600 mg to less than 0.3 mg in the resin phase, while iodide was retained. The same procedure was followed in the present study. Iodide was recovered subsequently by elution from the column.

Preliminary experiments on 300 mg of Deacidite FF resin indicated that 2 M ammonium nitrate solution eluted nearly 90% of the iodide within a volume of 10 ml, the remaining having been lost in the separation step. Experiments were carried out using 1 g of the indigenously available Tulsion A-27(Gel) anion exchanger in the NO<sub>3</sub>-form. The procedure consisted of loading the saline water sample (1 ml), removal of chloride and bromide with 10 ml of 0.2 M ammonium nitrate, followed by elution of iodide with 2 M ammonium nitrate (15 ml). The

**Table 1.** Elution of iodide from the column.

Weight of resin	: 1 g (NO <sub>3</sub> form)					
Loading volume	: 5 ml					
Volume per fraction of eluate	: 5 ml					
Elution of Cl <sup>-</sup> and Br <sup>-</sup>	: 5 ml 0.2 M NH <sub>4</sub> NO <sub>3</sub>					
Elution of iodide	: 5 ml fractions of 2 M NH <sub>4</sub> NO <sub>3</sub>					
	Iodide eluted in each fraction (%)					
Iodide loaded (ng)						Total (%)
	1	2	3	4	5	
200	7.6	71.5	18.1	2.9	0.7	100.8
500	7.7	71.2	16.2	3.8	0.9	99.8
1000	2.6	83.9	9.8	1.1	0.4	97.8

**Table 2.** Effect of chloride ion.

Iodide taken (ng)	Absorbance of Fe-CNS complex at 460 nm				
	No Cl <sup>-</sup>	1 mg Cl <sup>-</sup>	2 mg Cl <sup>-</sup>	3 mg Cl <sup>-</sup>	4 mg Cl <sup>-</sup>
0	0.750	0.734	0.742	0.750	—
5	0.640	0.631	0.618	0.595	0.551
10	0.533	0.489	0.450	0.470	0.450
15	0.353	0.353	0.345	0.331	0.334
20	0.313	0.310	0.290	0.261	0.261

Initial Ce(IV) concentration :  $1.4 \times 10^{-4}$  M  
 Initial As(III) concentration :  $7.0 \times 10^{-5}$  M  
 Temperature : 26.5°C  
 Duration of the reaction : 40 m

**Table 3.** Effect of nitrate ion.

Iodide taken (ng)	Absorbance of Fe-CNS complex	
	No NH <sub>4</sub> NO <sub>3</sub>	0.5 M NH <sub>4</sub> NO <sub>3</sub>
10	0.418	0.382
15	0.285	0.266
20	0.199	0.191
25	0.149	0.153

Temperature: 28.5°C                      Duration of reaction: 60 m

recovery by this method for varying amounts of iodide labelled with I-131 tracer is given in table 1.

Next, the effect of chloride and ammonium nitrate on the determination by the arresting method was studied. Tables 2 and 3 give the results.

#### 4. Results and discussion

The presence of upto 2 mg of chloride in the aliquot used for the determination does not affect the measured value more than 10%. Navada *et al* (1983) have found no interference from 200 ppm chloride. In view of the decontamination factor of nearly 2000 by this method, even samples containing tens of milligrams of chloride per ml can be analysed. Similarly, measurements in the presence of 0.5 M ammonium nitrate also indicate no appreciable effect on the measured value. This concentration of  $\text{NH}_4\text{NO}_3$  corresponds to what is expected in the solution used for the measurement, after the elution step.

A few water samples from the coastal areas of Tamil Nadu, containing 0.2 to 30 mg of chloride per ml, were analysed for iodide by the present method. The results are given in table 4. The first four samples containing 20–50 ppb of iodide were also analysed by neutron activation (Krishnamoorthy and Iyer 1983). The agreement between the results is satisfactory, considering the low levels of concentrations. It further establishes the validity of the separation method, since as much as 28 mg of chloride per ml, present in the sample, does not give a positive interference. In tap water, 0.5 ppb levels of iodide have been determined, and the values compare well with those by the neutron activation technique.

#### 5. Conclusion

The method of pre-separation and its determination by the catalytic method can be readily adopted in a field laboratory for samples containing 0.5 to 50 ppb of iodide and upto 30 mg of chloride per ml. As reported earlier, the method can be applied for the analysis of common salt also. The chemicals and the anion exchanger are indigenously available and the analysis involves only three steps, namely, (i) anion

**Table 4.** Analysis of water samples.

Code nos.	Chloride (mg/ml)	Conc. of Iodide in ppb	
		by this method	by N.A.A
<i>Saline waters-I</i>			
171	0.28	28	23
172	8.15	39	56
173	27.8	51	71
175	1.1	37	45
<i>Saline waters-II</i>			
33	n.a.	13	
52	n.a.	13	
53	n.a.	7	
75	n.a.	9	
<i>Tap water</i>			
1	—	0.5	0.5
2	—	1.2	0.8

n.a.: not available.

exchange, separation and elution, (ii) catalytic reaction and (iii) absorbance measurement.

The overall precision of the procedure by the arresting method was found to be 6% which compares well with the neutron activation analysis.

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