



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

The use of kinetic methods for the determination of ultra-trace amount of iodide in water

F.Z. Shtewi ^a, R.A. Mokhtar ^{b,*}, A. Al-Zawik ^a, S. Karshman ^a

^a Chemistry Department, Faculty of Science, Zawia, Libya

^b Chemistry Department, Faculty of Education, 7th April University, Zawia, Libya

Received 10 July 2009; accepted 10 July 2009

Available online 6 August 2009

Abstract A new method for the determination of ultra-trace amounts of iodide ion was developed. The proposed method employs ABTS, (2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonic acid)), as the chromogenic reagent, and made full use of the advantages of stopped-flow methodology. This method was found to be selective and sensitive. The method was based on the monitoring of the alteration in the rate of formation of the cation radical of ABTS by oxidation with chloramine-T using a stopped-flow system. Traces of iodide markedly increases the rate of the reaction. The alteration is proportional to the concentration of the iodide which can be determined over the range 0–50 ppb with an RSD of less than 0.5% over this range.

© 2009 King Saud University. All rights reserved.

1. Introduction

Iodine, as iodide is one of the trace elements present in some foodstuffs at below the 50 mg/kg level. It is generally regarded as one of the essentially nutritive elements. The analysis of iodine at trace and ultra-trace level is becoming increasingly important in the food industry (Holak, 1987; Van staden,

1986) and in the analysis of environmental samples such as natural waters. Attention has been growing to the role of iodide and bromide in the formation of trihalomethanes, which are regarded as possible carcinogens. Such trihalomethanes are formed during the oxidative treatment of drinking water (Verma et al., 1992). Several methods have been reported for the determination of iodide at ultra-trace levels, i.e. at ppb concentrations, viz: 10^{-7} M and below this concentration. Several different techniques have been employed.

A kinetic method (Vinas et al., 1987) for the determination of iodide in iodinated salt, based on the catalytic effect of iodide on the chlorpromazine-bromate reaction reported the limits of determination to be between 5 and 75 ppb. Other methods (Rubio and Perez-Bendito, 1989; Kenney et al., 1989) involved the effect of iodide on the cerium(IV)–arsenic(III) reaction. A spectrophotometric method (Truesdale and Smith, 2003) has been reported for the determination of iodide in river water over the range 20–100 ppb.

* Corresponding author.

E-mail address: faragshetewi@yahoo.com (R.A. Mokhtar).



A catalytic reduction method (Greenberg et al., 1992) was chosen in 1992 as a standard method for the range 20–60 ppb. Mitic et al. (2005) reported that a kinetic method for the determination of trace amounts of iodide by a catalytic effect on the oxidation of sodium pyrogallol-5-sulfonate by hydrogen peroxide. The reaction is followed spectrophotometrically at 436.8 nm, the calibration graph was found linear in the range 10–200 ppb (Mitic et al., 2005).

The inhibitory effect of iodide on the Pd(II) catalysed reaction between the EDTA–Co(II) complex and hypophosphite has been used in spectrophotometry, measuring the decrease in the absorbance at 540 nm. The range of determination reported was 2–28 ppb (Garcia et al., 1991). Iodide and thiosulphate have been determined using ion-pair, response for the iodide was over the range 10–100 ppb (Lookabaugh et al., 1987). Flow analysis technique was used for the determination of iodide ion at a nanogram level in water by Chandrawanshi et al. (2005). Iodide ion was also determined in urine and water samples using isotope dilution analysis. The range of determination reported in urine was 0.22–124.22 ppb (Unak et al., 1999).

Iodide has been separated from other species by oxidation to iodine element, extraction into carbon tetrachloride, re-conversion to iodide ion, reaction with methylene blue to form an ion-pair. Extraction of this ion-pair complex into 1,2-dichloroethane and spectrophotometric determination of the complex. The range of determination was 7.5×10^{-8} M to 3×10^{-6} M (KOH et al., 1988).

The use of a stopped-flow technique coupled with a fixed optics system capable of monitoring changes of 0.001 absorbance units has been previously reported (Mokhtar et al., 2008). It was considered that using this, coupled with a kinetic method based on a selective reaction and involving the formation of a colour, would have potential for the development of a method capable for the determination of ultra-trace amounts of iodide.

Consideration of potential chromogens indicated that the choice should be governed by the commercial availability of the chromogen in an analytical acceptable state of purity as well as using a substance that gave a product with a high molar absorptivity. The compound 2,2'-azinobis(3-ethylbenzothiazoline)-6-sulphonic acid (ABTS) is used as an indicator for redox titrations involving glucose. It is readily available in the required state of analytical purity and the product, the cation radical, is highly coloured in dilute solutions. This compound was chosen for further study and use in the proposed reaction sequences.

2. Experimental

A block diagram of the experimental layout is given in Fig. 1. Light from a 50 W tungsten-lamp passes through approximately 1 cm length of the water in the thermostatted water bath (to act as a heat filter). Then through the optical cell and an optical filter (to select the required wavelength), mounted on the side of the optical cell and then directly on to a focusing lens in front of a photodiode.

2.1. Signal output

The progress of the reaction is then followed by measuring the change in absorbance of the beam of monochromatic light. A

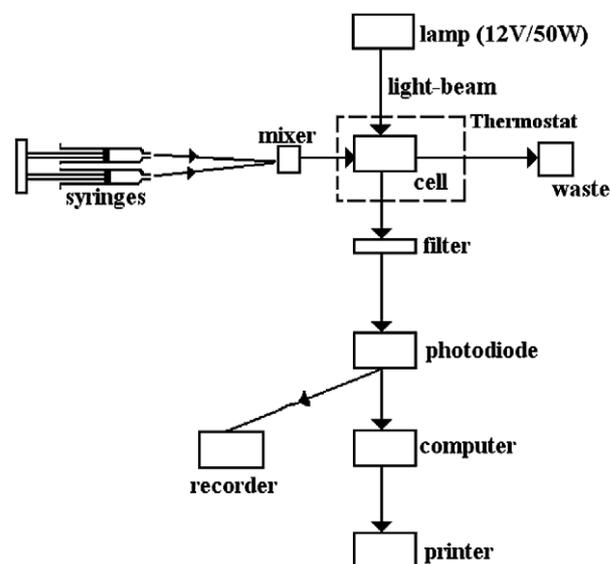


Figure 1 Block diagram of the stopped-flow system.

simple electrical circuit allows the signal to be amplified (sensitivity control) and zero-end on the scale by appropriate “back-off”. The electronically amplified signal from the detector is then recorded on a millivolt potentiometric recorder. If required, the signal can be further amplified using the recorder’s sensitivity control.

From the trace, suitable reaction parameters such as the initial rate of reaction can be calculated. Using the apparatus as presently designed it is possible to obtain 800% “back-off” and this is equivalent to using a recorder with a chart width of 2 m.

2.2. Dispensing of reagents

Glass syringes fitted with Hamilton stainless steel/teflon three-way valves were used. The pistons of both syringes are connected to a block which allows them to be operated singly or simultaneously. In practice, it was found that a volume of ca. 0.5 cm^3 , for each syringe was an acceptable volume for all experiments.

The reactants pass through separate coils of thin walled polyethylene delivery tubing (1 mm; length 80 cm; nominal volume 0.625 cm^3) immersed in the thermostatted bath ($\pm 0.5^\circ \text{C}$) and into a mixing chamber which causes homogeneous mixing by tangential action. From the mixing chamber the solutions pass immediately into an optical cell of 1.5 cm optical bath length, with an internal volume of approximately $0.14 \mu\text{l}$, permanently fixed in position. The solutions then pass to waste.

2.3. Reagents and solutions

2.3.1. Solution A

Chloramine-T solution (1.0×10^{-3} M).

2.3.2. Solution B

Solution B contains a mixture of fixed amounts of potassium iodide solution (i.e. 2.0 cm^3 ; 1.0×10^{-6} M) and ABTS solution

Table 1 Shows the variety of buffer solutions regarding the relative rate.

pH	7.0	7.2	7.4	7.9	8.4	9.0
Relative rate	4.5	3.2	1.7	0.02	0.01	0.0

(i.e. 2.0 cm^3 ; $1.0 \times 10^{-3} \text{ M}$). To this mixture various amounts of 0.1 M HCl were added in order to give different solutions with different ranges (i.e. in the range of 7–9).

Each solution was made up to 25 cm^3 with de-ionized water. The results are given in Table 1. A pH of 7.0 was chosen for further studies (see Section 4). A stock solution of pH 7 buffer, with a molarity of 0.02 M with respect to TRIS was prepared by dissolving 24.23 g of the solid in water, adding HCl (430 cm^3 ; 0.02 M) and diluting with water to 1 l .

3. Results and discussion

The effects of variations of the experimental parameters were investigated. The parameters which were individually varied and included: (i) pH of the system, (ii) concentration of the TRIS buffer used, (iii) concentration of the ABTS, (iv) concentration of the chloramines-T, (v) temperature of the reaction cell. In each set of experiments equal volumes (0.5 cm^3) of two solutions (A and B) were mixed in the stopped-flow apparatus and the absorbance of the solution in the reaction cell was monitored at 625 nm . The relative rates of formation of the green colour were calculated from the traces.

- (i) *Effect of varying the pH of the system:* The effect of variations in the buffer concentrations showing in Table 1.
- (ii) *Effect of variations in the concentration of the buffer:* The reaction cell thermostatted at $25 \pm 0.1 \text{ }^\circ\text{C}$. The results are shown in Table 2. A buffer concentration of $4 \times 10^{-2} \text{ M}$ was chosen for further work.
- (iii) *Effect of variations in the ABTS concentration:* A series of 25 cm^3 of solutions was prepared each containing potassium iodide solution (0.50 cm^3 of $1 \times 10^{-5} \text{ M}$) and TRIS buffer (10 cm^3 of 0.1 M ; pH 7.0). To each solution of the series 2 cm^3 of ABTS solution was added to have solutions of concentration ranging from 10^{-3} M to $2 \times 10^{-4} \text{ M}$. The final volume was completed to the mark with de-ionized water. A sample of each solution was mixed with Chloramine-T ($1 \times 10^{-3} \text{ M}$) in the thermostatted reaction cell. The initial slopes of the reactions were calculated and corrected for the blank. The results are given in Table 3.

The results obtained indicate an increase in the rate with increase in the concentration of the ABTS until a concentration of $2 \times 10^{-4} \text{ M}$ is reached. This concentration was selected for further work.

- (iv) *Effect of variations in the temperature of the system:* Each of a series of aliquots of an iodide solution containing 10 ppb was mixed with aliquots of the buffered ABTS reagent and then with aliquots of Chloramine-T to form a mixture. The initial rate of the reacting compounds of each mixture was monitored at different temperatures. The results obtained are shown in Table 4. From the data shown in Table 4, it appears that it is necessary to control the temperature of the reaction. A temperature of $25 \text{ }^\circ\text{C}$ was chosen.

An aliquot (0.5 ml) of a standard iodide solution (solution C) and an aliquot (0.5 ml) of the oxidant were simultaneously injected into the system and the course of the reaction was monitored at 625 nm for at least 60 s .

3.1. Calculations from the recorder output

It may be seen from typical traces (Fig. 2) that the slope of the “blank” reaction, i.e. the non-catalysed oxidation of the ABTS, depends upon the sensitivity employed to monitor the reaction. The initial rate of the reaction is calculated by measuring the slope and calculating the tangent of the angle to the horizontal. It is necessary to correct for any blank value. In practice it is found to be more convenient to allow the trace to continue for at least 60 s after the onset of the oxidation reaction. And then measure the intercept of the trace on the vertical axis of the chart at 60 s (or some other fixed time) after the onset of the oxidation reaction. This intercept is designated the $I_{(0)}$ intercept, or $I_{(t)}$ intercept (see Table 5).

From the recorder trace the initial rate of reaction and the $I_{(60)}$ values were calculated as indicated. The process was repeated for the series of solutions C and the rates of the reactions and the $I_{(60)}$ values were plotted against the concentration of iodide. The results are given in Table 6.

When the graph of the relative rate is plotted against iodide concentration a straight line plot with a linear correlation

Table 2 Shows the variety of TRIS buffer solutions regarding the relative rate.

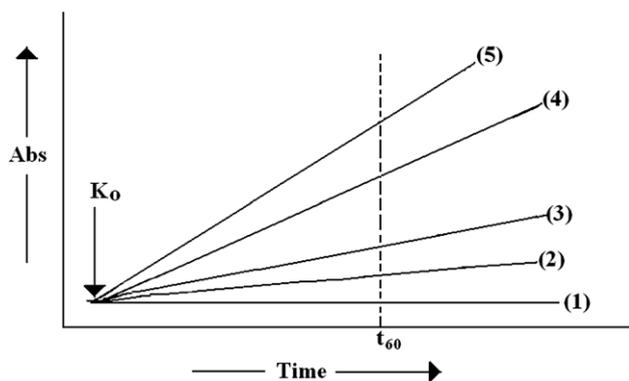
TRIS buffer conc. (10^{-3} M)	8	20	32	44	60
Relative rate	16.0	13.4	12.0	11.7	11.5

Table 3 Shows the ABTS concentrations regarding the initial rate.

Final conc. ABTS 10^{-5} M	2	4	8	12	16	20	24
Initial rate	1.3	2.5	5.0	7.3	9.7	11.0	11.0

Table 4 Shows the effect of temperature of the system.

Temp. (°C)	19	21	25	34
Initial rate	61.5	61.5	70	78

**Figure 2** Typical recorder traces of concentration of iodide in solutions (1) blank, (2) 2.0×10^{-8} M, (3) 4.0×10^{-8} M, (4) 1.0×10^{-7} M and (5) 1.4×10^{-7} M.

coefficient of 0.999 is obtained. A similar linear correlation exists between the intercept₆₀ and the concentration of the analyte.

3.2. Interferences

From the prepared calibration graph the initial rate of the reaction, (corrected for any blank value) Or: intercept on the vertical axis of the trace at 60 s. (or t s.) after the start of the reaction. [$I_{(60)}$ or $I_{(t)}$] (corrected for any blank value), can be calculated. If very low concentrations are to be monitored it may be necessary to allow the intervals of time for obtaining

the intercept to be up to 100 s. This allows the difference between the “blank” intercept and the analyte intercept to be seen. Table 6 shows the concentrations of the foreign species that can be tolerated without significant effect (less than 5% interference).

3.3. Removal of interferences

The interference of most of the cations is readily removed using a suitable cation exchange. However, the cation exchanger did not completely remove the interference caused by the addition of mercury (see Section 4).

3.4. Removal of the effect of mercury ions present

The above results indicate that the system can tolerate the presence of up to 2000 ppm of chloride ion without showing any effect on the determination of iodide. Attempts were made to eliminate the effects of mercury by addition of chloride to a sample. It was found that it is necessary to remove residual iodide from a commercial sample of A.R. sodium chloride by repeated recrystallisation (the results reported above are using iodide-free sodium chloride).

Using sodium chloride which had been twice recrystallised from water to remove any residual iodide. The following results shown in Table 7 were obtained in the analysis of water sample which containing 25 ppb of iodide and a set of samples which contained 25 ppb of iodide and 250 ppb of mercury(II).

The initial rate for the solution without mercury(II) present was 16.0.

3.5. Determination of an unknown sample

- (1) Use the same experimental conditions used in the calibration exercise. As shown in Table 8. Switch on the electrical systems and allow warming up for at least 5 min. Ensure that all controls are locked into the posi-

Table 5 Shows $I_{(60)}$ values were plotted against the concentration of iodide.

Conc. of iodide (10^{-8} M)	0	2.0	4.0	8.0	12.0	20.0	28.0
Relative rate	0	1.05	2.24	4.44	6.66	11.0	15.5
I_{60} , (mm) intercept	0	30.5	67.0	133	200	330	461

Table 6 Shows the concentrations (ppm) of the foreign species that can be tolerated without significant effect.

Anions	Iodate (K)	Bromide (K)	Bromate (K)	Chloride (Na)	Sulphate (Na)	Nitrite (Na)	Nitrate (Na)	EDTA (Na)		
Conc.	1000	300	1000	2000	1400	300	1000	170		
Cations	Ca(II)	Mg(II)	Fe(II)	Fe(III)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Pb(II)	Mn(II)
Conc.	2000	2000	5	20	5	500	400	1	200	900

Table 7 Shows the effect of addition of sodium chloride to a solution containing Hg(II) 250 ppb and 25 ppb of potassium iodide.

Conc. of Cl^- (ppm)	0	400	1200	2000	2800
Initial rate	9.0	12.0	15.0	19.9	16.0

Table 8 Conditions for the determination of iodide, and for calibration purposes, using the stopped-flow apparatus.

<i>Parameter</i>	<i>Instrument condition</i>
Wavelength	625 nm
Chart speed	60 mm per minute
Recorder sensitivity (mv for full scale deflection)	20 mv
Offset	800%
Temperature	In range 20–25 °C ± 0.1 °C
<i>Solution</i>	<i>Concentration</i>
Chloramine-T	1×10^{-3} M
Buffered reagent	ABTS (2×10^{-4} M) in pH 7.0 TRIS buffer

tions previously determined in the calibration sequence. Ensure that the interference filter, for monitoring the absorbance of the cell solution, is monitored at 625 nm.

- (i) If no cationic interferences are present, pipette 5 cm³ of the buffered ABTS reagent solution into a 25 cm³ flask. Make up to the mark with the sample. Shake the mixture to achieve homogeneity and place in the thermostat. Connect to the syringe B and flush out the syringe and coil by ejecting two aliquots (0.5 cm³) of the buffered ABTS and sample mixture through the system.
- (ii) If cationic interferences other than Hg(II) are present, pipette 5 cm³ of the buffered ABTS reagent solution into a 25 cm³ flask. Connect a 25 cm³ syringe filled with the sample to the ion-exchange column. Slowly eject the solution through the ion-exchanger into the flask, making the volume to the mark. Shake the mixture to achieve homogeneity and place the flask into the main thermostat. Connect to the syringe B and flush out the syringe and coil by ejecting 2 aliquots (0.5 cm³) of the buffered ABTS reagent and sample mixture through the system.
- (iii) If cationic interferences including mercury(II) are present, to 100 cm³ of the unknown sample add approximately 0.1 g of bromide free sodium chloride. Shake to dissolve the solid and to achieve homogeneity, then proceed as in (2)(ii).
- (3) Switch on the recorder.
- (4) With both syringes full, inject aliquots of the two solutions into the coils and hence to the mixing cell. Allow recording of the trace to continue for at least 60 s.
- (5) From the trace obtained, calculate: either, the initial rate of the reaction; or, the intercept on the vertical axis of the trace at 60 s. after the start of the reaction, ($I_{(60)}$).
- (6) Calculate the concentration of iodide in the sample using one of the previously prepared calibration curves.

4. Discussion

The main aim of the investigation was to design a selective and sensitive method for the determination of ultra-trace amounts of iodide present in water. An associated aim was to ensure that the method was simple and required both relatively low-cost reagents and equipment. The latter being such that on economic ground, it was suitable to become a dedicated instrumental system in general analytical laboratory used for routine or semi-routine assay of the chosen analyte.

The reason for the choice of the stopped-flow technique and a system involving the measurement of initial rates of the analyte reaction has been previously established. The fixed optical and physical geometries of the system ensure that the system is optically stable and capable of reproducing minute changes in the optical absorbance of the solution under investigation. Using the optical “backing off” system, with a “back-off” of 800% gives the equivalent of a chart width of approximately 2 m for a full scale deflection an ability to reproduce a single to 1 mm. Thus, the present apparatus is capable of reproducibly detecting and measuring absorbance changes of the order of 0.0001 absorbance units. This factor ensures that a sensitivity physical system is of relatively low-cost, easy to use and service and sufficiently robust in design to be used in a general laboratory by skilled or semi-skilled workers after the various reagents have been prepared.

When choosing a substance to be used as a selective and sensitive reagent for ultra-trace amounts of a particular analyte in aqueous media, the factors governing selectivity and sensitivity should not be separately considered. The choice of a chromogenic reagent which is selective towards the changes in the system is primarily governed by the type of analyte reactions available. In any selective determination of iodide, use may be made of the redox properties of the iodide/iodine system. This is especially so when other ions present may also undergo redox reactions. The use of the hypochlorite ion for the oxidation of iodide is well established. Its use in systems which have bromide present requires the control of the pH of the medium to decrease the probability of interference by the competing bromide/bromine system.

The choice of the pH was governed partly by the fact that any bromide present is less likely to be oxidized at this pH that is the iodide and also by the fact that mixing equal volumes of 0.1 M TRIS and 0.1 M HCl and diluting with water gives a buffer with a pH of approximately 7.0. Thus, a usable buffer is easily made by even unskilled labor and it is possible to dispense with the need to check the pH if all calibrations are done using such a mixture. A further consideration for choosing this pH is that at the chosen temperature (25 °C) the pK_a of TRIS is approximately 8.0 and thus alteration in the ionic strength of the solution when sodium chloride is added to sequester Hg(II) will not have a significant effect on the pH of the medium.

A result of any oxidative reaction involving the chromogen will be either two forms of the reagent (a leuco and a coloured form) or a new compound. In either case it is essential that there should be a fairly large difference in the molar extinction coefficients of the two compounds or forms so that small changes in the amount of the compound measured in the system are manifested as significant changes in absorbance.

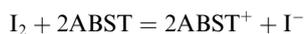
An oxidative is ABTS, which is an established chromogenic reagent, readily available in an acceptable state of purity, capable of being stored in normal laboratory conditions for months without deterioration. It gives a product with an acceptable high difference in its molar extinction coefficient to that of the parent compound.

When a solution of Chloramine-T is mixed with an iodide solution, buffered at pH 7.0 and containing ABTS, the almost colourless solution first becomes yellow and then quite rapidly turns a blue-green colour. The rapid formation of the yellow colour is explained by the formation of iodine from the iodide by its oxidation by Chloramine-T. The disappearance of the

Table 9 Comparison of methods for the determination of iodide in the concentration range 0–50 ppb.

Technique	Range (ppb)	% RSD
Spectrophotometry	2–28	2.2
Spectrophotometry	5–70	3.9
HPLC	3–1600	1.43
Colorimetry	20–80	NL
Potentiometry	10–400	2.7
Voltammetry	0.3–17	5.0
Flow injection	50–150	1.0
Proposed method	0.5–5.0	1.0
	2.5–36	0.3

yellow colour and the formation of the green colour of the cation radical of ABTS are explained as following:



In this way the iodide is regenerated to be re-oxidized by the HOCl. Thus, assuming the two reactions are rapid, there is practically little decrease in the original concentration of the iodide which can be regarded as acting as a “catalyst”. The rate of formation of the ABTS radical will be governed by the rate of formation of the iodine molecules and thus is indirectly governed by the initial concentration of the iodide ion.

Substances which remove iodide by complexation, such as mercury(II) or remove iodine by other redox reaction are potential sources of interference. However, the latter type of potential interferences is removed by the presence of the excess of Chloramine-T. Possible cationic interferences, other than mercury, may be removed by a suitable ion-exchange system. Mercury may be sequestered by taking advantage of the ability to form chloro-complexes of mercury which, although having lower stability constants than the iodo-complex, are formed because of the large excess of chloride used.

The proposed method may thus be used for a wide variety of samples of the types generally found in initial waters used for the generation of steam for boilers, etc. or for potable purposes. A comparison of the method with others reported for the determination of iodide at the ppb level is given below in Table 9.

When selecting a method for general industrial use in routine or semi-routine analysis, the range of any method may not be the only consideration. The overall cost per analysis is also important. This is governed by the cost of the apparatus and materials used and often more importantly by the cost of the labor involved. A method requiring many operational steps between receiving of sample and dispatching of the results may require the use of skilled (and thence expensive) labor. In many of modern industrial work analytical results are needed as fast as possible and often in a matter of minutes from receiving of sample. Apparatus which is expensive may not always be able to be dedicated to a particular analysis and thus time will be required setting up a method for semi-routine analysis, and overall time taking to obtain a result after receiving of the sample may be relatively long.

As stated, one of the aims of the present study was to design a method and procedure which is simple, robust and relatively low-cost. Consideration of the above methods indicates that this has been achieved. The voltammetric method requires a pre-concentration step before analyzing for the iodide and the concentration of the analyte in the material undergoing analysis is greater than 50 ppb. The colorimetric method uses 10 different

reagents in the procedure. The cost of HPLC equipment is much higher than that required for other methods. The flow injection method is reported to be able to deal with approximately 50 analyses per hour but no indication is given if these are analyses (done in at least duplicates) or are single results. In use as a routine assays (in duplicate) to be obtained per hour, (If interferences are present, the rate is reduced to about 20 per hour). The method of calculation, involving the use of fixed time intercepts, is both simple and rapid.

The proposed method uses low-cost apparatus, only a few reagents and dose not require any pre-concentration steps before the analyte is determined. The ability to vary the sensitivity of the system ensures that it may be used over various ranges of concentrations appropriate to the particular industrial problem.

After preparation of the solutions and calibration graphs, the method dose not requires the use of highly skilled labor and thus overall costs are reduced.

Thus, from various considerations, including ease of operating procedure, initial cost of equipment, running cost and the speed of analyses, the proposed method appears to have industrial potential. Fig. 2 shows the typical recorder traces of iodide in solutions regarding the following concentrations.

1-Blank (no iodide ion), 2– 2.0×10^{-8} M, 3– 4.0×10^{-8} M, 4– 1.0×10^{-7} M, 5– 1.4×10^{-7} M.

1 cm of original chart corresponds to 10 s.

T_{60} is time ordinate 60 s. after onset of oxidation reaction.

I_{60} is the intercept 60 s. after the onset of the oxidation reaction.

Note:

- (i) *Absorbance*: 1 cm of original chart corresponds to 0.001 a.u.
- (ii) For a concentration of 1.4×10^{-7} M, I_{60} corresponds to 0.017 a.u. with the parameters as indicated.

References

- Chandrawanshi, S.K., Chandrawanshi, S.K., Patel, K.S., 2005. *J. Autom. Method Manage. Chem.* 18 (5), 181.
- Garcia, M.S., Sanchez-Pedreno, C., Albero, M.I., Sanchez, C., 1991. *Analyst* 116, 653.
- Greenberg, A.E., Clesceri, L.S., Eaton, A.S., 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th ed. American Public Health association, Washington, pp. 4–72.
- Holak, W., 1987. *Anal. Chem.* 59, 2218.
- Kenney, R.O., Bator, J., Reading, C., 1989. *Anal. Biochem.* 179, 139.
- KOH, T., Ono, M., Makino, I., 1988. *Analyst* 113, 945.
- Lookabaugh, M., Krull, I.S., Lacourse, W.R., 1987. *J. Chromatogr.* 387, 301.
- Mitic, S.S., Miletic, G.Z., Kostic, D.A., 2005. *Anal. Sci.* 19 (6), 913.
- Mokhtar, R.A., Shtewi, F.Z., Al-Zawik, A., Karshman, S., 2008. *Jordan J. Chem.* 3, 305.
- Rubio, S., Perez-Bendito, D., 1989. *Anal. Chim. Acta.* 224, 185.
- Truesdale, V.W., Smith, P., 2003. *Analyst* 100, 111.
- Unak, P., Darcan, S., Yurt, F., Biber, Z., Coker, M., 1999. *Boil Trace Elem. Res.* 71–72, 463–470.
- Van staden, J.F., 1986. *Anal. Lett.* 19, 1407.
- Verma, K.K., Jain, A., Verma, A., 1992. *Anal. Chem.* 64, 1484.
- Vinas, P., Cordoba, M.H., Sanchez-Pedreno, C., 1987. *Talanta* 34, 351.

Further reading

- Myashita, M., Yamashita, S., 1990. *J. Chromatogr.* 498, 137.