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Analytical Methods Section

Determination of iodide in table salt by flow injection analysis using Pyrocatechol Violet

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A spectrophotometric flow injection method for the determination of iodide based on the catalytic effect of this ion on the oxidation of Pyrocatechol Violet by potassium persulphate was developed. The method allows the determination of 0·5–5 mg litre^{-1} iodide at a rate of 60 samples per hour and is subject to very few interferences. It was successfully applied to the determination of iodide in table salt.

INTRODUCTION

The interest in the determination of iodide in foodstuffs has grown considerably in the last few years on account of the well-known fact that iodine metabolism in humans plays a major role in the formation of thyroid hormone, of which healthy adults require *c.* 25 μg daily.

Because of the high concentration of iodine in sea water, marine vegetation, sea food and edible vegetables grown in coastal areas are particularly rich in this element.

Vegetables grown inland—and the tissues of animals that are fed them—typically contain little iodine as a result of the low content of this element in the water. This deficiency is usually corrected by including iodinated salt in human diet in order both to obtain the additional iodine supply required for an adequate intake of this element and to prevent goitre through deficient synthesis of thyroid hormone.

In this work a new flow injection procedure has been developed for the determination of iodine based on a kinetic spectrophotometric method originally devised by Yonehara *et al.* (1988) for the determination of bromide as a catalyst for the reaction between Pyrocatechol Violet and hydrogen peroxide in a mixed acid medium (HCl + H_2SO_4). The sensitivity of the determination increases with the HCl concentration used. The method was adapted to the determination of iodine and subsequently applied to the determination of this halide in table salt.

The analysis for iodide at low concentrations is usually carried out by using batch kinetic methods. One such method is based on the catalytic effect of iodide on the redox reaction between cerium(IV) and arsenic (III), which was first studied in detail by Sandell & Kolthoff (1934, 1937) and has subsequently been applied to the determination of this halide in waters (Dubravcic, 1955; Barkley & Thompson, 1960; Malmstadt & Hadjiioannou, 1963; Knapp & Spitzy, 1969; Truesdale & Smith, 1975), thyroid hormone (Müller *et al.*, 1953; Strickland & Maloney, 1957; Knapp & Leopold, 1974) and urine (Acland, 1957; Grases *et al.*, 1985). Other iodide-catalysed reactions have also been used to develop methods for the determination of this ion (Bognar & Nagy, 1969; Jasinskiene & Umbraziunaite, 1975; Sierra *et al.*, 1975, 1977; Kreingol'd *et al.*, 1978; Igov *et al.*, 1979; Sriramam *et al.*, 1983, 1987; Sánchez-Pedreño *et al.*, 1985; Viñas *et al.*, 1987; Yonehara *et al.*, 1989). However, there are few references to the analysis for iodide by flow injection analysis (FIA); most of them rely on potentiometric (Ilcheva *et al.*, 1989) or electrochemical sensing. On the other hand only a few of such methods involve spectrophotometric detection (Deguchi *et al.*, 1983; Miyazaki *et al.*, 1984; Tanaka *et al.*, 1985; Kamson, 1986; Al-Wehaid & Townshend, 1987), which is by far the most straightforward and frequently used analytical technique.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade and distilled water was used throughout. The solutions employed were as follows:

—A 1 g litre^{-1} iodide standard that was prepared by dissolving 0·1308 g of KI (Merck, PA) previously dried at 105°C for 2 h in distilled water and diluted to 100 ml in a volumetric flask. Working strength solutions were prepared daily by appropriate dilution with further distilled water.

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—A 12 g litre^{-1} $K_2S_2O_8$ solution made by dissolving 1·2 g of the product (Probus, RA) in distilled water and diluting to 100 ml in a volumetric flask.

—A 6 × 10^{-3} M stock solution of Pyrocatechol Violet (Fluka pro analysi) prepared by dissolving 231·8 mg of the dye in 100 ml of distilled water. This solution was used to make 250 ml of a more dilute (6 × 10^{-4} M) solution containing 3 M HCl by mixing 25 ml of the stock with the required volume of concentrated hydrochloric acid (Merck, PA) and then making to volume with distilled water.

Apparatus

A custom-built semi-automatic system including an IBM-compatible computer to control injection and acquire and process spectrophotometric data was used.

Figure 1 depicts the FIA configuration used, which consisted of an eight-way Gilson Minipuls 3 peristaltic pump, a Rheodyne 50 injection valve that was controlled through the computer via a mechanical actuator, a Techtron thermostatic bath and a Hewlett-Packard 8452A diode array spectrophotometer furnished with a flow cell of 18 μl volume and 10 mm path length. All reactors and the injection loop were made from poly(tetrafluoroethylene) (PTFE) tubing of 0·5 mm bore.

Data acquisition and processing

A computer program developed by the authors (Cladera *et al.*, 1991) was used to control the injection of standards and samples, as well as the acquisition and processing of the spectrophotometric data. The program takes full advantage of the potential of the HP 8452A diode array detector for the rapid acquisition of spectra and, optionally, also allows complete spectra to be acquired at every point along the FI recording and absorbances to be measured at different wavelengths. In this manner, oscillations in the refractive index arising from injection of a sample with a much greater ionic strength than the carrier can be readily corrected and FI recordings obtained by plotting the absorbance differences found at the maximum absorption wavelength of Pyrocatechol Violet (550 nm) and another where the dye does not absorb at all (700 nm). In any case, peaks arising from the aforementioned changes in the refractive index can also be avoided by injecting the sample into a carrier with a similar salt content. Both alternatives provide good results.

The program also automatically processes the FI recordings obtained by detecting peaks, locating the baseline, calculating peak heights and areas, constructing calibration graphs and determining the concentrations in the samples.

FIA procedure

The determination was started by setting the different reagent streams in motion along the FIA manifold in order to allow the background colour due to Pyrocatechol Violet to spread throughout. Once a constant absorbance was measured, 100 μl of sample or standard was injected into the carrier stream, which consisted either of water circulated at a flow-rate of 0·44 ml min^{-1} or an NaCl solution of the same concentration as the table salt sample, depending on whether refractive index oscillations were to be corrected by plotting absorbance differences or equalising the ionic strength of the carrier used with that of the injected sample.

After the preset residence time (53 s) had elapsed, a peak reflecting the effect of iodide on the oxidation of the dye was obtained. This effect was monitored through the absorbance decrease of Pyrocatechol Violet. The FI recording was stored in a computer file and subsequently processed in order to determine the peak height over the baseline and the injected sample concentration by interpolation of the height on the calibration graph.

RESULTS AND DISCUSSION

Optimisation of the flow injection system

Injection of the iodide solution into the FI manifold resulted in a decrease in the absorbance resulting from the catalytic effect of the halide on the oxidation of Pyrocatechol Violet by persulphate ion.

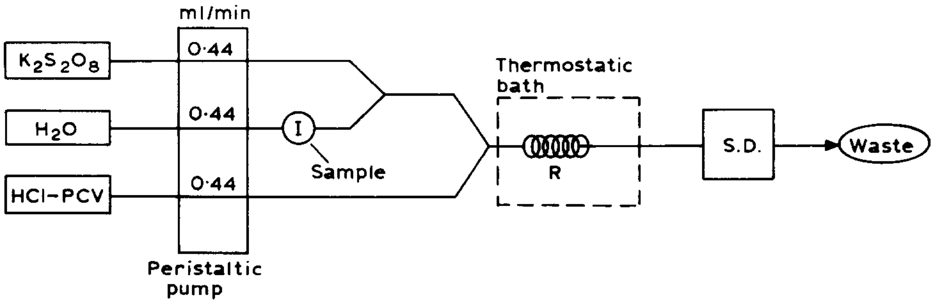

Fig. 1. FI manifold used for the determination of iodide. I, sample injector; S.D., spectrophotometric detector (λ = 550 nm); R, reaction coil (3 m); [$K_2S_2O_8$] = 12 g litre^{-1}; [HCl] = 3 M; [Pyrocatechol Violet] = 6·0 × 10^{-4} M; T = 55°C.

Various manifold designs were tried in order to avoid the peak resulting from water injection. The best results in this respect were obtained by using water as carrier (Fig. 1).

Effect of variables on the analytical reaction

The influence of the nature of the oxidant used was studied since the reagent originally employed for this purpose by Yonehara *et al.* (1988), viz. H_2O_2, provided rather an uneven baseline. Of the various oxidants tested, namely dissolved oxygen, Cu(II), Ce(IV), MoO_4^{2-}, VO_3^- and $S_2O_8^{2-}$, only the last yielded satisfactory results (a reasonably smooth baseline and taller peaks).

The oxidation of Pyrocatechol Violet by persulphate requires a highly acidic medium. Yonehara *et al.* (1988) recommended using a mixture of up to 0·59 M HCl and up to 0·43 M H_2SO_4. The effect of the various acid(s), viz. HCl, HNO_3 and H_2SO_4, was investigated and it was found hydrochloric acid alone gave the tallest peaks in the present study.

Figure 2 reflects the variation of the peak height with the concentrations of Pyrocatechol Violet, hydrochloric acid and potassium persulphate.

The influence of the HCl concentration was studied over the range 0·5–5·8 M. Reaction development was maximal for 3 M HCl, which was therefore chosen for subsequent experiments.

The effect of oxidant ($K_2S_2O_8$) concentrations between 5 and 24 g litre^{-1} was also investigated. As can be seen in Fig. 2, the signal obtained was maximal at a persulphate concentration of 12 g litre^{-1}.

Finally, the influence of the Pyrocatechol Violet was studied over the concentration range 1×10^{-4}–7×10^{-4} M. As can be seen in Fig. 2, the peak height increased with increase in the dye concentration up to 6×10^{-4} M, above which the measured absorbance was too high and detracted from baseline stability. This last concentration was thus chosen as optimal.

Influence of FI variables

In order to optimise the functioning of the FI manifold the influence of such variables as the reaction coil length, flow-rate, temperature of the thermostatic bath and injected sample volume were studied.

Figure 3 shows the influence of the reaction coil length, temperature and overall flow-rate. As can be seen, the coil length and temperature influenced the reaction development significantly. Three metres and 55°C were chosen as optimal since a longer length or higher temperature resulted in no added benefit.

The analytical signal obtained by using the above optimal coil length and temperature slightly increased with the overall flow-rate up to 1·32 ml min^{-1}, above which it started to decrease as a result of the decreased residence time of the injected sample. The above flow-rate was therefore chosen as optimal.

Finally, the peak height increased with increase in the injected sample volume between 50 and 150 μl. A

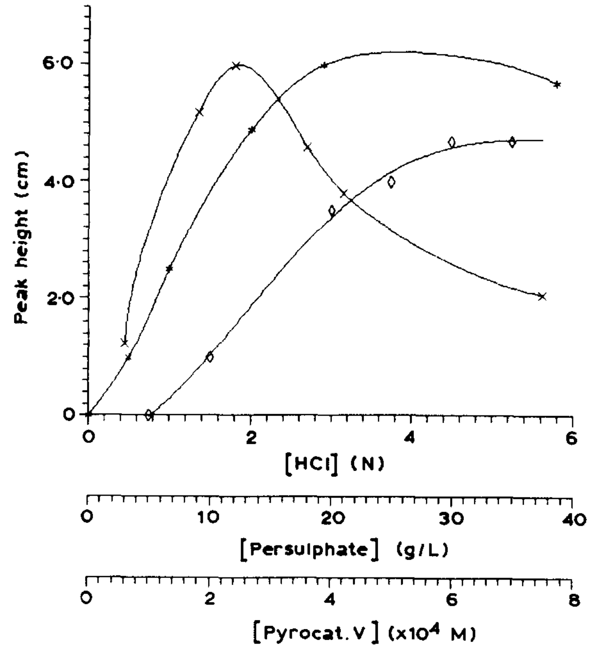

Fig. 2. Variation of the peak height with the concentration of: (a) HCl (*, [I$^-$] = 5 mg litre^{-1}; [$K_2S_2O_8$] = 8 g litre^{-1}; [Pyrocatechol Violet] = 5·0 × 10^{-4} M; T = 50°C; overall flow-rate = 1·7 ml min^{-1}; reaction coil length = 4 m); (b) Pyrocatechol Violet (◇ [I$^-$] = 1 mg litre^{-1}; [$K_2S_2O_8$] = 16 g litre^{-1}; [HCl] = 3 M; T = 50°C; overall flow-rate = 1·7 ml min^{-1}; reaction coil length = 4 m); (c) [$K_2S_2O_8$] (×, [I$^-$] = 1 mg litre^{-1}; [HCl] = 3 M; [Pyrocatechol Violet] = 5·0 × 10^{-4} M; T = 50°C; overall flow-rate = 1·7 ml min^{-1}; reaction coil length = 4 m).

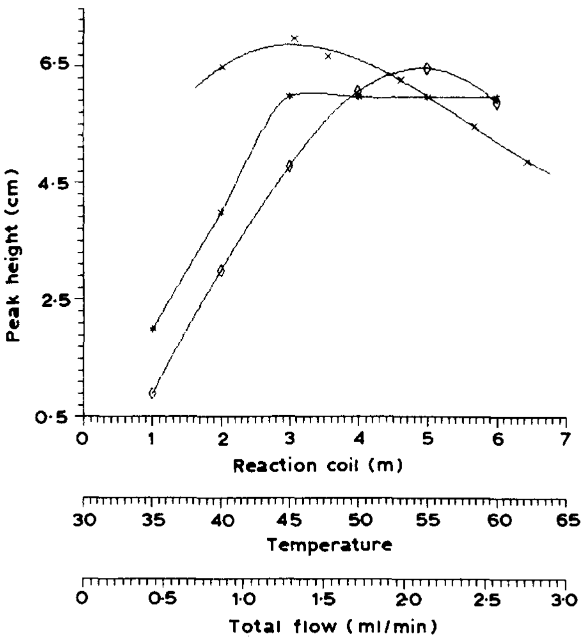

Fig. 3. Variation of the peak height with: (a) the reaction coil length (*, [I$^-$] = 1 mg litre^{-1}; [$K_2S_2O_8$] = 12 g litre^{-1}; [Pyrocatechol Violet] = 6·0 × 10^{-4} M; [HCl] = 3 M; T = 50°C; overall flow-rate = 1·7 ml min^{-1}; (b) temperature (◇, [I$^-$] = 1 mg litre^{-1}; [$K_2S_2O_8$] = 12 g litre^{-1}; [HCl] = 3 M; [Pyrocatechol Violet] = 6·0 × 10^{-4} M; overall flow-rate = 1·7 ml min^{-1}; reaction coil length = 3 m); (c) overall flow-rate (×, [I$^-$] = 1 mg litre^{-1}; [HCl] = 3 M; [Pyrocatechol Violet] = 5·0 × 10^{-4} M; [$K_2S_2O_8$] = 12 g litre^{-1}; T = 55°C; reaction coil length = 3 m).

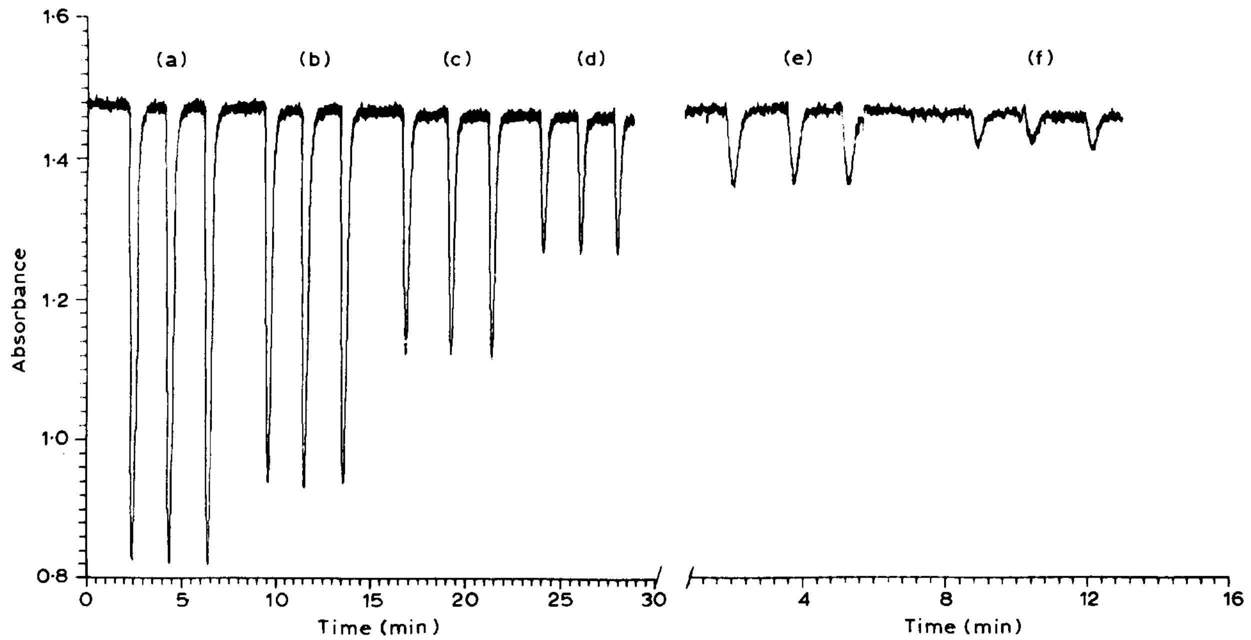

Fig. 4. Flow injection recording used to construct the calibration graph by triplicate injection of solutions containing iodide: (a) 6·0, (b) 4·0, (c) 2·0, (d) 1·0, (e) 0·5 and (f) 0·2 mg I litre^{-1}.

volume of 100 μl was chosen for subsequent experiments to avoid the peak broadening and hence the reduced sample throughput arising from the use of larger volumes.

Under the above optimal conditions, the dispersion coefficient, D (Ružička & Hansen, 1988), was found to be 4·5 and the throughput achieved was 60 samples per hour.

Determination of iodide

Calibration graphs

Under the above optimal conditions, the linear determination range for iodide was 0·5–5 mg litre^{-1} and the detection limit was 0·3 mg litre^{-1}. The equation of the calibration curve was $A = 0{\cdot}039 + 0{\cdot}131C$ ($r = 0{\cdot}985$, $n = 6$), where C is the iodide concentration in mg litre^{-1}. The detection limit was calculated according to IUPAC's recommendations (Long & Winefordner, 1983). Figure 4 shows six points of the FI recording obtained. The precision of the method for 1 mg litre^{-1} iodide, expressed as the relative standard deviation (RSD), was 4% ($p = 0{\cdot}05$, $n = 10$).

Table 1. Effect of interferents on the determination of iodide

Species	Tolerated concentration (mg litre^{-1})
Ca^{2+}, Mg^{2+}, NH_4^+, Al^{3+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, K^+, Mn^{2+}, NO_3^-, SO_4^{2-}, F^-, EDTA, tartrate, CN^-	100*
Br^-	75
Fe^{3+}	20

[Dye] = 6 × 10^{-4} M; [HCl] = 3 M; [$K_2S_2O_8$] = 12 g litre^{-1}; [I^-] = 5 mg litre^{-1}.
Maximum tolerated deviation = ±2σ.
* Maximum assayed concentration.

The linear determination range can be broadened by using a lower temperature. Thus, such a range extended between 5 and 25 mg litre^{-1} at 45°C, the corresponding calibration equation being $A = 0{\cdot}016 + 0{\cdot}034C$ ($r = 0{\cdot}990$, $n = 6$).

Effect of foreign ions

The effect of potential interferents was studied by adding them in different proportions to an iodide solution containing 5 mg litre^{-1} of the analyte. The results obtained are listed in Table 1. A given ion was considered to interfere with the determination if it resulted in a signal variation greater than ±2σ. As can be seen from the table, only Fe(III) showed a serious interference at a concentration only four times that of iodide. Attempts at circumventing this interference by masking the iron with EDTA, cyanide, fluoride, tartrate and citrate were unsuccessful. In any case, the proposed method is quite selective towards iodide ion overall.

Applications

The proposed method was applied to the determination of iodide in iodinated table salt with no sample

Table 2. Determination of iodide in iodinated table salt. (Results expressed as μg KI per g salt)

	Volumetric method[a]	FIA	
		Standard addition[b]	Calibration curve[b]
Sample 1	81	85 ± 4[c]	83 ± 2
Sample 2	174	180 ± 6	173 ± 2

[a] Average of four determinations.
[b] Average of three determinations.
[c] Deviation expressed as s.d.

pretreatment. The iodide concentration in the assayed samples was high enough for the method to be implemented at 45°C, which provided a linear determination range of 5–25 mg litre^{-1}.

Table 2 lists the results obtained both by interpolation on the calibration curve, by the standard-addition method and by using a reference volumetric method (Spanish UNE, 1974). As can be seen, all three sets of results are quite consistent.

CONCLUSIONS

The proposed method is a useful alternative to the routine determination of iodide ion in table salt. It features reasonably good sensitivity and selectivity, and a high sample throughput as a result of the need for no sample pretreatment—only sample dissolution with water is required.

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