ORIGINAL RESEARCH

Determination of iodide using flow injection with acidic potassium permanganate chemiluminescence detection

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ABSTRACT: A simple and rapid flow-injection method is described for the determination of iodide, based on potassium permanganate chemiluminescence detection via oxidation of formaldehyde in aqueous hydrochloric acid. The calibration graph was linear over the range $1.0–12 \times 10^{-6}$ mol/L ($r^2 = 0.9955$) with relative standard deviations ($n = 4$) in the range 1.0–3.5%. The detection limit (3σ) was 1.0×10^{-7} mol/L, with sample throughput of 120/h. The effect of interfering cations [Ca(II), Mg(II), Ni(II), Fe(II), Fe(III) and Pb(II)] and anions (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, F^- and SO_3^{2-}) were studied. The method was applied to iodized salt samples and the results obtained in the range $0.03 \pm 0.005–0.10 \pm 0.006$ mg I/g were in reasonable agreement with the amount labelled. The method was statistically compared with the results obtained by titration; no significant disagreement at 95% confidence was observed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: flow injection analysis; acidic potassium permanganate; chemiluminescence; iodide; iodized salts

INTRODUCTION

Iodine is an essential part of the thyroid hormones that play an important role in the development of brain function and cell growth. Iodine deficiency causes serious delays in neurological development (1–4). An excess of iodine or iodide (>20 mg/day) can cause goitre and hypothyroidism as well as hyperthyroidism (5, 6). The World Health Organization recommends a daily iodine intake of 50–200 µg and in 24 h urinary excretion is less than 50–99 µg/L in endemic areas (7). To ensure that the correct amounts of iodine are added, the sensitive and rapid determination of trace amounts of iodine/iodide in natural waters, foodstuffs and biological samples is of great importance.

The catalytic properties of iodide have largely been explored as a means for its quantification. Deguchi *et al.* (8) used iodide catalysis of the cerium(IV)/arsenic(III) reaction and Fuchs *et al.* (9) used the reaction of iodate with *p*-aminophenol. Iodate oxidizes *p*-aminophenol to a quinoneimine, which immediately condenses with a second *p*-aminophenol molecule to give a blue indamine dye, measured at 540 nm.

Various flow-injection (FI) methods have been reported for determining traces of iodide in environmental, biological and iodized salt samples, based on spectrophotometry (8, 10–13), spectrofluorimetry (14)

and amperometry (15, 16). A chemiluminescence (CL) detection system has been found to provide rapid and sensitive methods for trace metals and anions, due to its transient nature. The luminol-CL system has been used to determine iodine in pharmaceutical products, employing a gas-diffusion unit (17). The limit of detection for iodine was found 0.8 µmol/L. However, ascorbic acid caused serious interference. Burguera *et al.* (18) described a FI method for iodide determination in urine samples, using the luminol-Co(II)-CL system with a limit of detection of 0.08 µmol/L and sample throughput of 3/h. Fujiwara *et al.* (19) recently reported an improved FI method for the determination of iodine using the luminol-CL reaction in a reversed micellar medium of cetyltrimethylammonium chloride in 1-hexanol-cyclohexane. A detection limit of 0.05 ng/cm^3 is achieved for iodine.

Potassium permanganate in acidic medium has been widely used as a reagent to generate CL with analytical applications in pharmaceutical, environmental, food, clinical and beverage samples at very low concentrations (20, 21). The potassium permanganate–formaldehyde CL system has been reported for the determination of iodine and iodide by means of their inhibition and enhancement effects (22, 23), with a detection limit of 7.87×10^{-7} mol/L and 1.8×10^{-7} g/mL, respectively. However, some of these methods have poor detection limit, low sample throughput, being nonspecific and involving toxic organic solvents.

In the present study we report a simple and rapid FI-CL method for the determination of iodide, based on aqueous acidic potassium permanganate as the CL

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reagent. Iodide enhances the oxidation of formaldehyde in the presence of the permanganate-CL reagent. Manifold parameters have been optimized and the method applied to the determination of total iodide in iodized salt samples, with a detection limit of 1.0×10^{-7} mol/L and sample throughput of 120/h.

EXPERIMENTAL

Reagents and solutions

All solutions were prepared using ultra-high purity (UHP) water (18.2 MΩ/cm, Elgastat, Maxima, UK) and all reagents were of analytical grade, supplied by Merck BDH, unless stated otherwise. Iodide stock solution (0.1 mol/L) was prepared by dissolving 1.66 g in 100 mL UHP water. Standards were prepared in water by serial dilution whenever required. Potassium permanganate stock solution (0.01 mol/L) was prepared by dissolving the required amount of compound in UHP water, filtered and stored in the dark. Diluted solutions were prepared by mixing portions of the stock solution with the required amount of HCl (0.2 mol/L). Fresh solutions were prepared weekly. Formaldehyde solution (1.5 mol/L) was prepared by diluting 24 mL commercially available formaldehyde solution (12.6 mol/L) to 200 mL with HCl (0.2 mol/L). Stock solutions (1000 mg/L) of cations [Ca(II), Mg(II), Ni(II), Fe(II), Fe(III), Pb(II)] and anions (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^-, F^- and SO_3^{-2}) for interference studies were prepared in UHP water from their respective salts and various working solutions were prepared from these stock solutions in UHP water. Iodized salt samples were collected from National Foods Ltd, Utility stores (Pakistan) and E. Merck (Germany).

Instrumentation and procedures

Figure 1 shows a flow-injection chemiluminescence manifold used for the determination of iodide. A peristaltic pump (Ismatec Reglo 100, 4 channels, Swit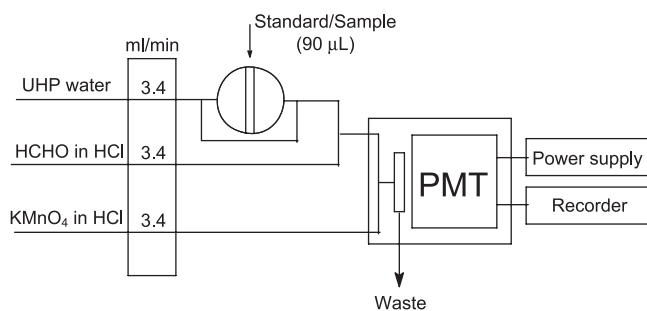zerland) was used to deliver the sample carrier and reagent solutions at a flow rate of 3.4 mL/min. A rotary injection valve (Rheodyne 5020, Anachem, Luton, UK) was used to inject iodide standards (90 μL) into an aqueous stream and merged with a stream of formaldehyde (1.5 mol/L in 0.2 mol/L HCl). This stream was then merged at a T-piece with the chemiluminescence reagent stream ($KMnO_4$, 2.0×10^{-5} mol/L). The merged stream travelled 3.0 cm before passing through a glass spiral flow cell (1.1 mm i.d, 130 μL internal volume) placed directly in front of an end-window photomultiplier tube (PMT, 9798QA, Electron Tubes, Ruislip, UK). The PMT, glass coil and T-piece were enclosed in a light-tight housing (24). The PMT was attached to a 1 kV power supply (Electron Tubes, PM20SN, UK). The detector output was recorded using a chart recorder (Kipp & Zonen BD 40, Holland).

RESULTS AND DISCUSSION

Optimization of the FI manifold

In order to establish the optimum conditions for the determination of iodide, various parameters were investigated using a univariate approach. The key parameters optimized were hydrochloric acid, potassium permanganate and formaldehyde concentrations, sample volume, flow rate of sample carrier and reagent streams (see Table 1). All of these studies were performed using a 1.0×10^{-5} mol/L iodide standard solution and a PMT voltage of 1000 ± 5.0 V.

The efficiency of potassium permanganate CL is highly dependent on acid conditions, and typically gave a higher response at 0.2 mol/L HCl (range studied, 0.01–0.3 mol/L). The effect of potassium permanganate concentration was studied over the range 5.0×10^{-6}–5.0×10^{-5} mol/L, using the optimized hydrochloric acid conditions. The CL response increased up to 2.0×10^{-5} mol/L potassium permanganate (used in all subsequent experiments), above which the response decreased. The influence of formaldehyde concentration on the determination of iodide was studied over the range 0.1–2.5 mol/L and gave a maximum CL response at 1.5 mol/L.

Figure 1. Flow-injection chemiluminescence (FI-CL) manifold for the determination of iodide.

Table 1. Ranges investigated and optimized conditions for FI-CL manifold parameters

Parameter	Range	Optimized
HCl (mol/L)	0.01–0.3	0.2
$KMnO_4$ (mol/L)	5×10^{-6}–5×10^{-5}	2×10^{-5}
HCHO (mol/L)	0.1–2.5	1.5
Flow rate (mL/min)	0.5–4.2	3.4
Injection volume (μL)	30–180	90

The effect of flow rate and sample volume on the CL response was investigated in terms of sensitivity; speed and reagent consumption and the results are shown in Table 1. A flow rate of 3.4 mL/min gave the maximum CL response (range studied, 0.5–4.2 mL/min) with a steady baseline and reproducible (<2.0% RSD) peak height, and was used subsequently for all three channels. Similarly, a sample injection volume of 90 μL gave almost the highest CL response and was used for economy of sample consumption and speed of response respectively.

Analytical figures of merit

A calibration data of CL intensity vs. (I^-) over the range $1.0-12 \times 10^{-6}$ mol/L is given in Table 2 with the correlation coefficient ($r^2 = 0.9955$, $n = 7$) and regression equation $y = 0.7307x + 0.175$ [y = CL intensity (mV), x = concentration (μmol/L)]. The relative standard deviation (RSD) was 1.0–3.5% ($n = 4$) over the range studied. The limit of detection (3σ) was 1.0×10^{-7} mol/L iodide with a sample throughput of 120/h.

Table 2. Calibration data for iodide ($n = 4$)

Iodide ($\times 10^{-6}$ mol/L)	Mean of CL response (mV)	RSD (%)
Blank (UHP water)	0.04	2.5
1.0	1.1	3.5
3.0	2.3	2.0
5.0	3.5	2.2
7.0	5.0	1.6
9.0	6.7	1.2
12.0	9.1	1.0

Interferences

The effect of potential interferences on the blank response (in the absence of iodide) and on the determination of iodide (at 2.0×10^{-6} mol/L iodide) is given in Table 3. The cations Ca(II), Mg(II), Ni(II) and Pb(II) had no significant effect. Iron(II) (0.1 mg/L) and Fe(III) (1.0 mg/L) had an enhancing effect on both the blank signal and the iodide response. Interference from these cations was eliminated by iminodiacetate chelating resin (Chelax 100, 50–100 mesh, sodium form, Sigma) (25). The anions, chloride, sulphate, phosphate, nitrate, fluoride and sulphite had no significant effect. However, nitrite (10 mg/L) had a suppressive effect on the CL blank response and the iodide signal gave a negative response. This effect can be eliminated by using an on-line anion exchange mini-column.

Effect of salinity on the CL response

The effect of salinity on the CL response for iodide (2.0×10^{-6} mol/L) was investigated in the range 0.01–0.5 mol/L NaCl, prepared in UHP water, and the results are given Table 4. When injecting NaCl solutions (in the absence of iodide) as the blank, a small, gradual increase in the CL response was observed. The effect of NaCl on the determination of iodide was then characterized using 2.0×10^{-6} mol/L iodide in the range of NaCl standards. From low to high salinity, a small gradual increase in response was observed compared with UHP water. Sodium chloride (0.5 mol/L) was also used as the carrier in place of UHP water and iodide standards ($1.0–12 \times 10^{-6}$ mol/L) prepared in NaCl (0.5 mol/L) was injected into the sodium chloride stream. The baseline was noisy and reproducibility was poor compared to UHP water

Table 3. Effect of diverse ions on the determination of iodide ($n = 4$)

Name	Concentration (mg/L)	Response without iodide (mV)	Response with iodide (2.0×10^{-6} mol/L) (mV)
Blank (UHP H_2O)	0	0.04	1.94
Cations			
Ca^{2+}	100	0.2	2.0
Mg^{2+}	75	0.0	1.8
Ni^{2+}	1.0	0.1	2.0
Fe^{2+}	0.1	6.8	8.8
Fe^{3+}	1.0	0.3	2.3
Pb^{2+}	1.0	0.2	1.8
Anions			
Cl^-	1000	0.1	1.8
SO_4^{2-}	300	0.1	1.8
PO_4^{3-}	2.0	0.05	1.9
NO_3^-	30	0.1	2.0
NO_2^-	10	-ve	-ve
F^-	1.0	0.1	1.8
SO_3^{2-}	0.1	0.4	2.2

Table 4. Effect of salinity on the determination of iodide (*n* = 4)

Salinity (mol/L)	Iodide ($\times 10^{-6}$ mol/L)	CL response (mV)	RSD (%)
Blank (UHP H_2O)	0	0.03	2.5
0.01	0	0.05	2.7
0.05	0	0.1	3.0
0.1	0	0.2	2.5
0.2	0	0.5	3.7
0.3	0	0.7	1.8
0.4	0	1.0	2.0
0.5	0	1.2	1.5
0	2.0	1.8	1.8
0.01	2.0	1.9	2.0
0.05	2.0	2.0	1.9
0.1	2.0	2.2	2.0
0.2	2.0	2.4	1.6
0.3	2.0	2.6	1.3
0.4	2.0	2.8	1.7
0.5	2.0	3.0	1.2

Table 5. FI-CL determination of iodide contents in three iodized table salts (*n* = 5)

Sample	Iodide labelled (mg/g)	Proposed method (mg/g)	Titration method* (mg/g)
1	0.095	0.1 ± 0.006	0.11 ± 0.004
2	0.10	0.095 ± 0.008	0.10 ± 0.006
3	0.025	0.03 ± 0.005	0.032 ± 0.004

*Ref. (13).

as a carrier stream. The results demonstrate a salinity effect on the blank as well as on iodide determination.

Application to iodized salts

The proposed method was applied to the determination of iodide in iodized table salts. All samples were oven dried at 110°C overnight and stored in a desiccator until constant weight was obtained. 1.0 g from each sample was dissolved in UHP water (100 mL) and filtered through a Whatman filter paper No. 42. Prior to analysis, 25 mL each sample was treated with iminodiacetic acid chelating resin (Chelax-100, 50–100 mesh, sodium form, Sigma, USA) to remove any traces of metal cations, especially iron(II), which seriously affects the results at trace level (1.0×10^{-9} mol/L, unpublished data) and then injected directly into the FI-CL manifold for iodide determination. The results obtained for the three samples were in reasonable agreement with the amount labelled. The results were also compared statistically with those given by the titration method, as shown in Table 5. No significant difference was found between the results of the two methods at the 95% confidence limit.

CONCLUSION

The proposed FI-CL method for iodide determination is simple, rapid (120/h) with a detection limit of 1.0×10^{-7} mol/L as compared to previously reported methods (22, 23). Interfering cations present in iodized salt, especially iron(II) at low levels (nanomolar), was removed by chelating resin. The method was applied to iodized salt samples and the results compared were in reasonable agreement with the titration method.

Acknowledgements

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