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Application of the thermal lens effect for determination of iodide*

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Abstract—A new method for the determination of trace amounts of iodide has been developed by using the thermal lens effect. The ion-pair complex formed from iodide with ethyl violet was measured using a single beam thermal lens experiment with a He-Ne laser as a light source. The sensitivity of the method for determining iodide is 10^2 times higher than that of conventional spectrophotometry using the same colorimetric reaction. The detection limit of iodide is 50 pg. The method proposed has been applied to the determination of iodide at ppb levels in natural waters.

Keywords: iodide; thermal lens effect; He-Ne laser; ethyl violet; analysis.

1 Introduction

The thermal lens effect, first reported by Gordon *et al.* (Gordon, 1965), has been developed as a new tool for trace level determination. The first analytical application of the thermal lens effect was carried out for the determination of copper using a colorimetric reaction with EDTA (Dovichi, 1979). Recently, the thermal lens effect for the determination of iron (Imasaka, 1980), cobalt (Deng, 1980), uranium (Beithoud, 1983), neodymium (He, 1988), thallium (Zan, 1989), mercury (Lu, 1989), cobalt and antimony (Wu, 1992), antimony (Du, 1993) have been studied. Spectrophotometric determinations of nonmetal ions have also been accomplished using the thermal lens effect, such as nitrite (Fujiwara, 1982), phosphorus and arsenic (Grishko, 1984), perchlorate (Wu, 1992). All the methods mentioned above have demonstrated that the detection of thermal lens effect has become one of the most sensitive spectrometric method.

In the present work, a single beam system for thermal lens effect measurement of iodide is reported. The color development was based on the ion-pair formation of iodide with ethyl violet. The maximum absorbance (620 nm) of ion-pair extraction is close to the 632.8 nm output of He-Ne laser and it is suitable for the determination of trace iodide. The detection limit is 50 pg of iodide which is 100 times lower than conventional spectrophotometry using ethyl violet as color reagent (Chen, 1990). The method developed has been applied to the determination of iodide in natural waters at ppb levels. The results of analysis were in agreement with those obtained by ion

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chromatography and gas chromatography using butanol as a derivative reagent.

2 Experimental

2.1 Reagents

Standard iodide solution (1 mg I^-/ml) was prepared by dissolving 0.1307g of potassium iodide in water and diluting to 100 ml. Sodium nitrite solution (0.5%) was prepared by dissolving 0.5g sodium nitrite in 100 ml water and stored in refrigerator, the solution was prepared fresh weekly. Ethyl violet solution (0.1%) was prepared by dissolving 0.1g ethyl violet in 100 ml water. Potassium chloride solution (20%). Phosphoric acid solution (7.3 mol/L) was prepared by diluting 50 ml of concentrated phosphoric acid to 100 ml with water. Toluene was redistilled before use. All reagents were of analytical - reagent grade. Deionized and redistilled water were used.

2.2 Apparatus

A block diagram for the thermal-lens experimental system based on a single beam method is shown in Fig. 1. A helium - neon laser (LA, λ=632.8 nm) was used as a light source, the output power was stabilized to 30 mW and the beam was focused with a 15 cm focal length biconvex lens (CO). The laser beam was modulated by a chopper (LC) which was placed at the beam waist of the laser. The position of a 2 cm path length sample cell (SC) was adjusted to optimize the measurement. The intensity at the beam center was preamplified by the combination of a pinhole (PI, 1 mm) and a photodiode (PD). The signal was sampled and processed by a microcomputer system.

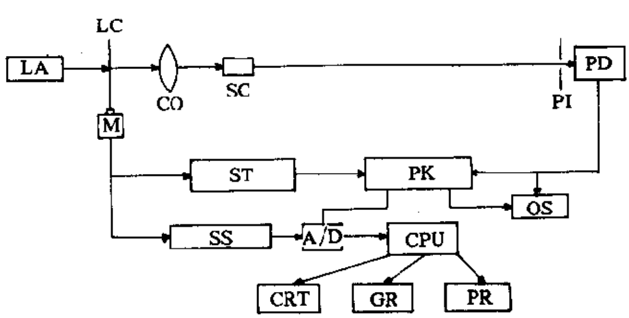

Fig. 1 Block diagram of the device for measurement of the thermal lens effect
LA: He - Ne laser; LC: light chopper; CO: convex; SC: sample cell; PI: pinhole; PO: photodiode; PH: peak holding circuit; ST: synchronizing trigger circuit; SS: synchronous sampling circuit; GR: Graphical recorder; PR: printer; OS: osilloscope; MO: motor

2.3 Procedure

The determination of iodide proceeds as follows. A certain amount of standard iodide solution (containing 0.1 μg I^-/ml) or water sample was pipetted into a separatory funnel. The following solutions were added in turn: 0.1 ml of 0.1% ethyl violet solution, 1 ml of 20% potassium chloride solution, 0.1 ml of 0.5% sodium nitrite solution and 0.6 ml of 7.3 mol/L phosphoric acid solution. Then the total volume of the solution was made to 5 ml with water. The final reaction mixture was mixed well, and extracted with 1 ml toluene for one minute. After the phase separation, discarded the aqueous phase, the organic phase was ready for measurement.

A 5 ml of toluene was pipetted into a 2 cm sample cell, after a blank measurement was made, a series of 50 μl portion of the organic phase was added to the cell with a microsynringe, the solution was mixed, allowed to stand for 1 min and the thermal lens effect measurement was made.

3 Results and discussion

3.1 Absorption spectrum

The absorption spectrum of ion-pair complex formed from iodide with ethyl violet is shown in Fig. 2. The maximum absorbance of the ion-pair complex is located at 620 nm, which is close to the 632.8 nm line of He-Ne laser. Hence, this color reaction is suitable for determination of trace iodide using the thermal lens effect.

3.2 Effect variables

The conditions for the color development, such as acidity of phosphoric acid, the amount of sodium nitrite, potassium chloride and ethyl violet were studied in detail. The optimum acidity of phosphoric acid was found to be 0.3—0.9 mol/L (Fig. 3). The optimum amounts of 0.5% sodium nitrite solution and 20% potassium chloride solution were 0.1—0.175 ml, 0.4—1.0 ml, respectively. Increasing the amount of 0.1% ethyl violet solution, the signal was increased. 0.1 ml of the solution was chosen because of lower reagent blank and higher signal.

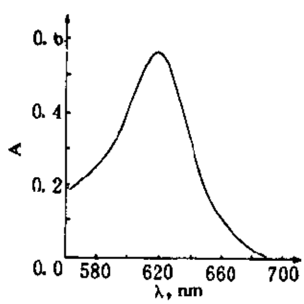

Fig. 2 Absorption spectrum curve

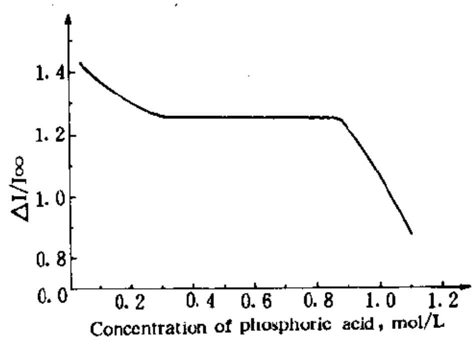

Fig. 3 Effect of phosphoric acid concentration

3.3 Effect of diverse ions

The effects of various amounts of diverse ions on the determination of 50 ng of iodide were examined. The addition of 2000 fold of phosphate, sulfate, nitrate, fluoride and chloride ions, tartaric acid, ascorbic acid, and 500 fold of bromide, sodium, potassium ions as well as 2 fold of mercury (II) ions did not interfere. Copper(II), cobalt(II), iron(II) and cadmium(II) ions interfered.

3.4 Calibration curve

The calibration curve obtained from standard solutions of iodide according to the proposed procedure is shown in Fig. 4. The linear range of iodide is 5—25 ng/ml toluene, and the detection limit is 50 pg of iodide. The coefficient variation is 9.4% ($n=5$) for 9.3 ppb iodide solution.

3.5 Analysis of iodide in natural water samples

The results of the iodide determined in the samples are given in Table 1.

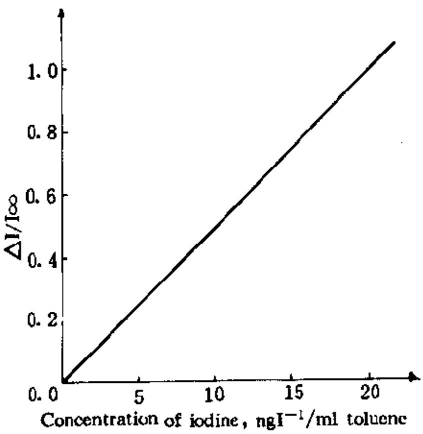

Fig. 4 Calibration curve of iodide

Table 1 Concentration of iodide in samples

Samples	I^- found in sample, μg/L	
River water	12.5	11.4*
Tap water	7.4	6.5*
Rain - water # 1	5.9	5.3**
Rain - water # 2	11.6	11.0**

* Results obtained by ion chromatography

** Results obtained by gas chromatography using butanol as derivative reagent

4 Conclusion

The method described for determination of iodide using the thermal lens effect is highly sensitive. The sensibility enhancement is 10^2 times as compared with spectrophotometry using the same color reaction. The method has been applied to determination of iodide in natural waters at ppb levels. The results of analysis of iodide are in good agreement with the values obtained by the method of ion chromatography and gas chromatography.

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