Kinetic Determination of Iodide Based on its Effect on the Hydrogen Peroxide Oxidation of Triflupromazine

Ashraf A. Mohamed

Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo 11566, Egypt

Summary. A new selective, sensitive, and simple kinetic method is developed for the determination of trace amounts of iodide. The method is based on the catalytic effect of iodide on the reaction of triflupromazine (TFP) with H₂O₂. The reaction is followed spectrophotometrically by tracing the oxidation product at 498 nm within 1 min after addition of H₂O₂. The optimum reaction conditions are TFP (0.4 × 10⁻³ M), H₂SO₄ (1.0 M), H₃PO₄ (2.0 M), and H₂O₂ (1.6 M) at 30°C. Following this procedure, iodide can be determined with a linear calibration graph up to 4 × 5 ng cm⁻³ and a detection limit of 0.04 ng cm⁻³, based on the 3 Sb criterion. The method can also be applied to the determination of iodate and periodate ions. Determination of as little as 0.2, 1.0, 2.0, and 4.0 ng cm⁻³ of I⁻, IO⁻³, or IO⁴⁻ in aqueous solutions gave an average recovery of 98% with relative standard deviations below 1.6% (n = 5). The method was applied to the determination of iodide in Nile river water and ground waters as well as in various food samples after alkaline ashing treatment. The method is compared with other catalytic spectrophotometric procedures for iodide determination.

Keywords. Catalytic spectrophotometric determination of iodide; Hydrogen peroxide triflupromazine reaction; River and ground waters; Food samples.

Introduction

Iodine is an essential nutrient in human diet that is naturally found in or added as a supplement to many food samples [1–3]. A recommended daily allowance of 150–200 μg I⁻ was adopted in the USA as well as European and many other countries. Deficiency of iodide leads to goiter disease, and excessive intake may contribute to thyrotoxicosis [1]; therefore, the determination of iodide in natural waters and food samples is important with respect to environmental and biochemical aspects.

Sensitive techniques for the determination of trace amounts of iodide include neutron activation analysis (NAA) [4, 5], inductively coupled plasma-mass spectrometry (ICP-MS) [6, 7], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [8, 9], and ion chromatography (IC) [10, 11]. Typical detection limits of 0.1–0.2, 1.0–9.0, 40.0–470.0, and 0.1–0.8 ng cm⁻³ (or ng g⁻¹) have been

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a Present address: Department of Chemistry, Faculty of Science, King Khalid University, Abha 9033, Kingdom of Saudi Arabia. E-mail: aamohammd@hotmail.com
reported for these methods. However, the high instrumental costs [4–9] and the need for pre-concentration [4–11] and/or separation [4–6, 10, 11] are common disadvantages.

On the other hand, kinetic methods of analysis [12–43] are simple and low-cost alternatives for iodide determination. Among them, the very sensitive Ce(IV)-As(III) [2, 12–16] and NO$_2$-[Fe(SCN)]$^{2+}$ reactions [16–19] have been frequently used, the former reaction having been adopted as a standard method for iodide determination in natural and waste waters and in food and biological samples [2, 12]. However, a high between-laboratory relative standard deviation has been frequently reported for that method [2, 3, 15–16]. This might be partly attributed to the limitations of the method to quantitatively detect or tolerate iodate ions that are found in natural waters and/or formed during the ashing steps of food samples [2, 3]. Therefore, a reverse-phase ion-pair liquid chromatographic method has replaced that method for I$^{-}$ determination down to 20 ng cm$^{-3}$, where iodide has been detected electrochemically with a silver working electrode at 0–50 mV [2]. However, the need for a low-cost, rapid, more sensitive, and selective method is still acute.

Triflupromazine (TFP), 2-trifluoromethyl-10-(3-dimethylaminopropyl)-phenothiazine, is a well-known tranquilizing, antihistaminic, and antipsychotic phenothiazine derivative. In presence of oxidizing agents, TFP is first oxidized to an orange-red radical cation (TFP$^+$) which is further oxidized to a colorless sulfoxide derivative (TFPS) in the presence of excess oxidant. TFP$^+$ shows a strong absorption maximum at 498 nm, whereas that of TFPS is found at 344 nm [44, 45]. Iodide ions exert a pronounced catalytic effect on the H$_2$O$_2$-TFP reaction that is reported here for the first time. It led to the development of an extremely sensitive and selective kinetic method for the determination of trace amounts of iodine that was conveniently applied to various water and food samples. The developed method is especially well suited to the analysis of small environmental and food samples.

**Results and Discussion**

*Effects of reaction parameters*

In acidic media, oxidizing agents readily react with TFP to give an orange-red species that is believed to be a radical cation, TFP$^+$, whose colour intensity and stability is greatly influenced by acidity [44, 45]. Thus, among the different acids tested, sulfuric acid gave measurable rate values at concentrations higher than 0.5 M as shown in Fig. 1. However, at H$_2$SO$_4$ concentrations above 1.5 M, the linearity of the A-t graphs for the catalyzed reaction became poor. Therefore, 1.0 M H$_2$SO$_4$ was used for preliminary investigations. The method being subject to severe interferences from trace amounts of Fe(III), Cu(II), and Mn(II) ions, phosphoric acid was also added to suppress these interferences by formation of stable complexes. The rates of the catalyzed and uncatalyzed reactions, $k_c$ and $k_u$, increased with phosphoric acid concentration. However, at concentrations above 2.5 M, the linearity of the A-t graphs became poor. Thus, 2.0 M, H$_3$PO$_4$ was used. Finally, a mixed acid solution of 1.0 M sulfuric and 2.0 M phosphoric acid was adopted in the recommended procedure.