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Determination of iodide by detection of iodine using gas-diffusion flow injection and chemiluminescence

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Abstract

This work describes development of a flow injection (FI) system for determination of iodide, based on the chemiluminescence (CL) reaction between iodine and luminol. Iodide in the sample zone is oxidized to iodine. Employment of a gas-diffusion (GD) unit allows for selective detection of the generated CL (425 nm). Preliminary results showed for concentrations of less than 2 mg L^{-1}, that signals were irreproducible and that the calibration was not linear.

In order to solve these problems, a method of 'membrane conditioning' was investigated, in which iodide stream was continuously merged with oxidant to generate I_2 that conditioned the GD membrane and tubing. This minimized surface interaction between the active surface and the I_2 generated from the samples, thus improving both precision and sensitivity. By employing membrane conditioning, it has been possible to reliably detect concentrations down to 0.1 mg L^{-1}.

At the optimized condition, an excellent linear calibration (r^2 = 0.999) was obtained from 0.1 to 1.0 mg L^{-1}. The method was successfully applied to determine iodide in some pharmaceutical products such as potassium iodide tablets and a liquid patent medicine. However, for vitamin tablets, ascorbic acid was found to interfere seriously by causing a negative signal.

Keywords: Chemiluminescence; Gas-diffusion; Iodide; Flow injection; Pharmaceutical products

1. Introduction

Iodine is an essential nutrient in the human diet. Iodine compounds are found in many foods, both naturally and added as supplements. Iodine compounds are also used in preparations of some pharmaceutical products. For example, iodine in the form of tri-iodide is used as antiseptic and disinfectant, while potassium iodide is thought to act as an expectorant. Iodine, mostly in the form of potassium iodide, is also used as an ingredient in multi-vitamin supplements. In the United States, potassium iodide is available in tablet form and sold in drug store for thyroid protection, in the event of nuclear emergency.

However, the level of iodine should be used with extreme caution in cases where patients are markedly sensitive to iodide [1]. In patients with hyperthyroidism, iodide rapidly inhibits the synthesis of thyroid hormones. Therefore, it is essential to have accurate and precise methods available to determine the iodine content of these pharmaceutical products.

Flow injection (FI) analysis [2] is a technique that provides the means of achieving reproducible automated analyses, and there have been several reports in the literature of the use of FI methods for the determination of iodide based on spectrophotometric [3], potentiometric [4], catalytic spectrophotometric [5–10] and flame atomic absorption spectrophotometric [11] detection methods. Determinations based on chemiluminescence (CL) emission from the iodine–luminol reaction have also been reported [12–15]. CL detection is attractive

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in terms of the relatively low cost of the equipment involved and the simplicity of the detection system. Moreover, the CL method permits very low detection limit for iodine down to 1×10^{-7} M [12]. Iodide does not react with luminol, and it is therefore necessary to first oxidize iodide to elementary iodine, in order to initiate chemiluminescence. According to previous reports, this CL detection may be susceptible to a number of interferences including metal ions, and for this reason, a separation technique is usually carried out before the analysis of real samples [13,14].

Burguera and others have reported use of a headspace device coupled to a FI system to separate iodine from the matrix before CL detection [13]. Fujiwara et al. proposed the use of on-line oxidation and solvent extraction coupled with reversed micellar mediated CL detection for determination of iodine and iodide in commercial gargle products [15]. In their work, oxidation of iodide to iodine and solvent extraction of iodine were performed simultaneously before CL detection using the reaction of iodine with luminol in a reversed micellar solution of hexadecyltrimethylammonium chloride.

Normally, by incorporating gas-diffusion (GD) into a FI system, volatile analytes can be separated from interferents in the sample matrix via diffusion across the hydrophobic membrane. This process is fairly selective because fewer species are converted to the gaseous form at room temperature [16]. Motomitzu and Yoden, for example, have reported the use of a tubular GD unit for determination of iodide and other halides [17], and Hakedal and Egeberg [18] used a GD–FI system for determination of iodide in brine. In this latter system, the absorbance of tri-iodide in the UV-region was measured for calibration.

We recently reported work based on the use of GD with a flow injection system for quantitative analysis of iodide [19]. However, the sensitivity of this system was limited by the photometric detection of the I_3^-–starch complex, and therefore in this present work, we have utilized the CL reaction between iodine and luminol as the means of detection. Some problems, which are caused by the chemical properties of iodine and the membrane, are described along with appropriate solutions. The potential of the CL–FI system for quantitative analysis of iodide in pharmaceutical samples is presented.

2. Experimental

2.1. The FI manifold

Fig. 1 depicts two FI systems, which were used in the method development. An AS-90 series autosampler (Perkin-Elmer, USA) was used for automatically loading standard or sample solutions into a 300 μl PTFE loop (1.0 mm i.d.). A FIAS-300 module (Perkin-Elmer, USA) was employed for pumping the reagents. A Metrohm gas-diffusion unit (model 754, Switzerland), fitted inside with a circular PTFE membrane (47 mm i.d., 0.8 mm thickness with pore size 0.45 μm; Sartorius, Germany), was employed. The unit consisted of

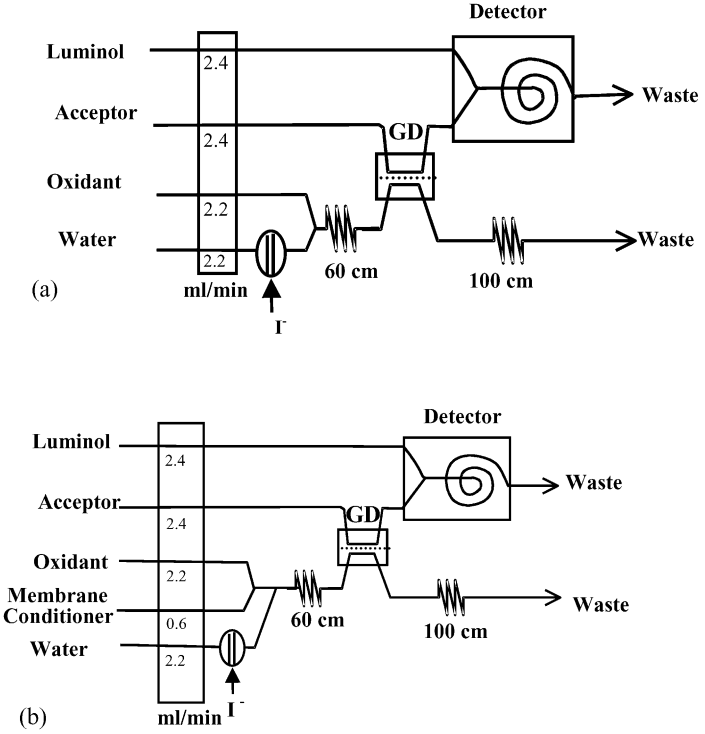

Fig. 1. Flow injection manifold used (a) in the preliminary method for determination of iodide and (b) applied to real sample analysis. Luminol: 7.5×10^{-4} M luminol in 0.1 M NaOH, Acceptor: 2% (w/v) KI solution, Oxidant: 0.01 M $K_2Cr_2O_7$ in 15% (v/v) H_2SO_4, Membrane conditioner: KI solution at 2 mg L^{-1}, GD: gas-diffusion unit, Detector: photomultiplier tube with a home-made flow cell.