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ScienceDirect
Chinese Chemical Letters 20 (2009) 1483–1486
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Simultaneous determination of fluorine and iodine in urine by ion chromatography with electrochemical pretreatment

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Received 26 March 2009

Abstract

A new method for the simultaneous determination of fluorine and iodine in urine by ion chromatography (IC) with electrochemical pretreatment has been developed. The pretreatment was performed in a novel electrochemical oxidation–neutralization device (EOND), in which iodide of the sample was oxidized to iodate and the alkaline digestion sample solution was neutralized. Under the optimized conditions, the limits of detection (LOD, S/N = 3) were 2.5 μg/L for fluoride and 20 μg/L for iodate, respectively. The recoveries were in the range of 93–102% for fluoride and 86–98% for iodate.

Keywords: Fluorine; Iodine; Urine; Electrochemical pretreatment; Ion chromatography

The determination of fluorine and iodine in urine is important for estimating the necessary supply in humans and is of great interest in toxicological research. There is a wide range of published methods for the determination of fluorine and iodine in urine [1–5]. Among them, ion chromatography (IC), with good selectivity and sensitivity, has attracted considerable attention and several detection modes have been used for urine analysis [6–9]. However, as for conductivity detection, the most popular mode, there is a lack of report on the determination of iodine, especially on the simultaneous determination of fluorine and iodine.

In this work, a novel electrochemical oxidation–neutralization device (EOND) was designed to oxidize iodide to iodate and neutralize the alkaline digestion sample solution, so that the simultaneous determination of fluorine and iodine in urine could be carried out by IC with suppressed conductivity detection.

1. Experimental

Eluents, standard solutions and reagent solutions were all prepared with ultrapure water of 18.2 MΩ cm. All chemicals used were salts and were of analytical-reagent grade. Eluents and solutions were filtered through 0.45 μm membrane prior to use.

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.05.030

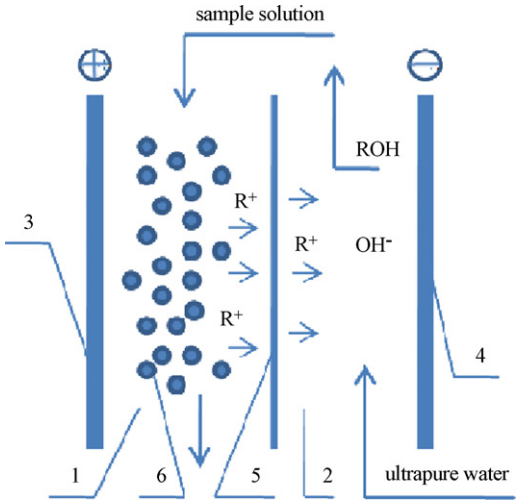

Fig. 1. Structure of the EOND. (1) Anode chamber, (2) cathode chamber, (3, 4) noble-metal electrode, (5) cation-exchange membrane and (6) high-capacity cation-exchange resin.

The IC system comprised a Shimadzu LC-10AT pump (Kyoto, Japan), a model 7725i valve injector with a 20 μL loop (Rheodyne, USA), a NJ-SA-4A anion-exchange column (Chinese Academy of Agricultural Sciences Institute of Plant Protection, Beijing, China), a model 732 IC conductivity detector (Metrohm, Switzerland) equipped with a DZS-3A suppressor (Xiamen University, Xiamen, China) and a LabNet data system (Xiamen Najing Instrument Co., Xiamen, China).

The fresh urine samples of healthy volunteers were decomposed in alkali according to the classical dry decomposition procedures [10,11], and the alkaline digestion sample solution was pretreated by the EOND designed below before IC analysis.

The diagrammatic view of the EOND is shown in Fig. 1. It comprises two thin PTFE chambers: anode chamber (1) and cathode chamber (2), each with a porous noble-metal electrode (3, 4) and separated by a piece of cation-exchange membrane (5). The anode chamber is packed with the high-capacity cation-exchange resin (6).

When it works, a dc potential is applied between the anode and cathode. The sample solution is pumped through the anode chamber and it undergoes the following electrolysis at the anode:

$$I^- + 6OH^- - 6e^- = IO_3^- + 3H_2O \quad (1)$$

$$4OH^- - 4e^- = 2H_2O + O_2(g) \quad (2)$$

Here, iodide in the sample is oxidized to iodate and the alkaline digestion sample solution is neutralized, meanwhile, the ultrapure water is pumped through the cathode chamber and it undergoes the following electrolysis at the cathode:

$$2H_2O + 2e^- = H_2(g) + 2OH^- \quad (3)$$

The product of electrolysis, OH^- combines with the cations, which are forced to move through the cation-exchange membrane from the anode chamber, to form waste alkali and finally is removed.

2. Results and discussion

After the sample reaction mixture was dissolved, the concentration of the residual alkali was very high. Loading the unpretreated sample into IC caused large baseline shift, which interfered the peak of fluoride, moreover, the concentrated alkaline increased the eluting power, making the retention time of fluoride shorter, as shown in Fig. 2(a). This degraded the determination accuracy and sensitivity of fluoride. In addition, iodide in the solution was polarizable, and under the common chromatographic conditions with conductivity detection, long retention time, low sensitivity and poor peak shape made its analysis unvalued. By using the EOND, the residual alkali could be neutralized, so good baseline and accurate retention time of fluoride were achieved. Meanwhile, iodide could be

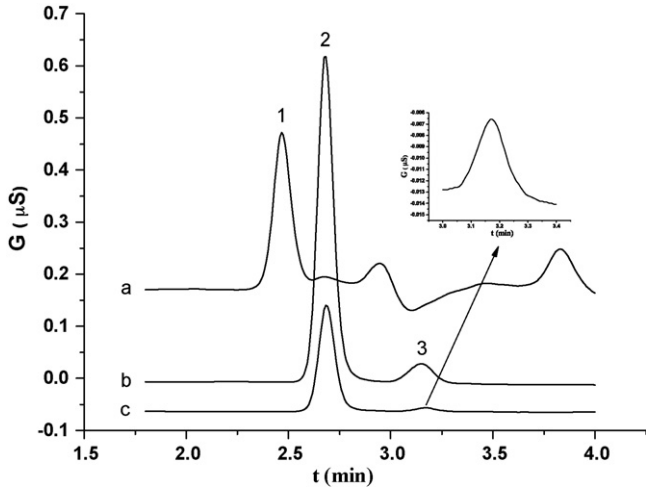

Fig. 2. Chromatograms of the unpretreated sample (a) and the pretreated samples with (b) and without (c) addition of 0.3 mg/L fluoride and 0.2 mg/L iodate. Peak identification: (1, 2) fluoride and (3) iodate.

oxidized to iodate, which was eluted easily, thus better peak shape and lower detection limit were obtained, as seen in Fig. 2(c). During the pretreatment process, no chemicals but only ultrapure water was used, so no interferential ions were introduced.

Parameters affecting the separation efficiency and detection sensitivity, such as flow rates of the electrolytes, electrolysis currents, sorts of anion-exchange columns, concentrations of eluents, etc., were investigated in detail. A NJ-SA-4A anion-exchange column was chosen in the separation process. The eluent was 4 mmol/L $Na_2B_4O_7$ at a flow rate of 2.0 mL/min. In addition, experiments also showed that the sample solution at a flow rate of 0.5 mL/min in the EOND and with the electrolysis current density of 19.1 mA/cm^2 could give above 98% oxidation efficiency and complete neutralization.

Under the optimized conditions, the response linearity, the detection limit, and the reproducibility of two analytes were examined. The calibration curves were linear from 0.05 to 10 mg/L for fluoride and from 0.1 to 10 mg/L for iodate, respectively. The calibration equations and correlation coefficients were: $y = 693.28x - 121.53$ with the r of 0.9995 for fluoride and $y = 8210.2x - 414.4$ with the r of 0.9996 for iodate in terms of peak area response. Detection limits of 2.5 μg/L for fluoride and 20 μg/L for iodate were obtained (S/N = 3). The precision was studied by assaying two concentration levels of the standard solution: 0.5, 5 mg/L of fluoride and 0.3, 3 mg/L of iodate. The relative standard deviations (RSD) of fluoride and iodate were 0.8% and 1.5%, respectively.

The proposed method was applied successfully to the determination of fluorine and iodine in human urine. The typical chromatograms of the pretreated samples with (b) and without (a) addition of 0.3 mg/L fluoride and 0.2 mg/L iodate were shown in Fig. 2. It was found that the contents of fluoride and iodate in human urine were 0.39 ± 0.03 mg/L and 0.24 ± 0.05 mg/L, and the recoveries of the two analytes varied from 93% to 102% for fluoride and 86% to 98% for iodate, respectively.

3. Conclusion

A novel electrochemical oxidation–neutralization device was designed to oxidize iodide to iodate and neutralize the alkaline sample solution. It was applied successfully to the simultaneous determination of fluorine and iodine in urine by IC.

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