Food Chemistry 117 (2009) 461–465

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Short communication

Analytical application of food dye Sunset Yellow for the rapid kinetic determination of traces of copper(II) by spectrophotometry

Snežana S. Mitić [a], Ružica J. Micić [b,*], Ranko M. Simonović [b]

[a] Department of Chemistry, Faculty of Sciences and Mathematics, University of Nis, Visegradska 33, 18000 Nis, Serbia
[b] Faculty of Sciences and Mathematics, University of Priština, Lole Ribara 29, 38220 Kosovska Mitrovica, Serbia

ARTICLE INFO

Article history:
Received 13 August 2008
Received in revised form 12 April 2009
Accepted 13 April 2009

Keywords:
Copper determination
Kinetic method
Food samples
Sunset Yellow

ABSTRACT

A sensitive and rapid kinetic method for trace determination of Cu(II) was developed and validated, based on its catalytic effect on the oxidation of disodium-6-hydroxy-5-[(4-sulphophenyl)azo]-2-naphtalenesulphonic acid (wide used, food colour “Sunset Yellow FCF”, E110, in text selected as SY) by hydrogen peroxide in borate buffer at pH 10.5. The reaction was monitored spectrophotometrically by measuring the decrease in the absorbance of SY at 478.4 nm. The optimum operating conditions regarding concentration of reagents, pH and temperature were established. The calibration curve was linear up to 318 ng mL^{-1} of Cu(II) and the limit of detection ($3\sigma/S$) is 5.0 ng mL^{-1}, and limit of quantification ($10\sigma/S$) is 16.67 ng mL^{-1}. The proposed kinetic procedure was successfully applied to monitoring of the concentration of Cu(II) in fruit, wine and milk samples from different areas. The results obtained by the proposed kinetic procedure were compared by those obtained by ICP-OES method, and shown good agreement. The proposed kinetic method could be used for monitoring of quality of drinks or fruit depending on Cu(II) concentration, because of its important role as nutritional element.

1. Introduction

Since copper occurs at low concentration in many real samples, such as natural, tap, waste waters, food, wine, drinks and soil, a sensitive, cost-effective, selective and rapid method is required for its determination in those samples. Copper is essential to human health, but only in limited amounts (Prasad & Halafihi, 2003).

In many food samples and drinks (fruit, juices, milk and wines) copper and iron are widely present. The high concentration of Cu, Fe, Mn and Zn may cause instability and turbidity of wine (Liskovskii & Skurikhin, 1976). Typical wines contain average copper levels at about 0.1–0.3 mg L^{-1} (Li, Guo, & Wang, 2008). In wines, the main sources of copper are equipments used in the wine production, addition of copper salts ($CuSO_4$) and pesticides employed during growth.

Hydrogen peroxide may be formed during the oxidation of phenols in wine, which has been widely accepted (Li et al., 2008). H_2O_2 in association with iron and copper tends to generate reactive oxygen species such as hydroxyl radical ($^{\cdot}OH$), which is known as the Fenton reaction (Li et al., 2008). In that way, most of the $^{\cdot}OH$ radicals generated in wine and fruit juice samples come from the metal-catalysed decomposition of hydrogen peroxide according to the Fenton-type reaction.

In recently reported references, Cu(II) was determined in different samples by using graphite furnace atomic absorption spectrometry (GF-AAS), (Ajtony et al., 2008; Karadjova, Izgi, & Gucer, 2002), inductively coupled plasma optical emission spectrometry (ICP-OES), (Lara, Cerutti, Sajonia, Olsina, & Martinez, 2005; Moreno et al., 2008). High performance liquid chromatography (Bermejo et al., 2001; Katerina, Christian, Ilse, Gregory, & Josef, 1999), and anodic stripping voltammetry (Cesar, Joanna, Jon, & Richard, 1999; Zeng, Liu, Tan, Zhang, & Gao, 2002) have also been used for the determination of copper with high sensitivity and selectivity, but suffer from more or less time consuming procedures and complicated instrumentation.

Despite of the instrumental improvements of the last decades, spectrophotometric techniques (Reddy, Reddy, Narayana, & Reddy, 2008) are still attractive from an analytical point of view since they are cheap, sensitive and simple to implement in laboratories. Among them, the kinetic-catalytic methods give high sensitivity and accuracy without the need for expensive and special equipment, by using different masking reagents or extraction to improve their selectivity (Crespo, Andrade, Inon, & Tudino, 2005; Crouch, Cullen, Schelline, & Kirkor, 1998; Crouch, Schelline, & Kirkor, 2000; Ghasemi, Kiaee, Abdolmaleki, & Semnani, 2008; Mitic, Miletic, & Obradovic, 2004; Mottola & Perez-Bendito, 1996; Prasad & Halafihi, 2003; Tomiyasu, Aikou, Anazawa, & Sakamoto, 2005; Tosic, Mitic, Obradovic, & Sunaric, 2004). Their sensitivity is at least 2–3 orders of magnitude higher than that of the ordinary

---

* Corresponding author.
E-mail address: ruzicamicic@yahoo.com (R.J. Micić).

0308-8146/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2009.04.042

spectrophotometric methods. Catalytic-kinetic methods have been widely used in determining many species at traces levels.

Some of them have low sensitivity (Ghasemi et al., 2008; Tosic et al., 2004), or poor selectivity, which makes difficulties in their application in complex samples. Compared to other kinetic methods for the determination of Cu(II), the kinetic method developed in this work falls to order of more sensitive methods (nanogram levels). Among its high sensitivity, the method has also advantage in view of its simple and rapid applicability to different real samples, using easy available masking agents for elimination main interfering effects (Fe^{3+}, Mn^{2+}, Ni^{2+} and Co^{2+}), without complicated pretreatments, with satisfactory accuracy which was confirmed by ICP-OES method.

In this study, we found that food dye SY is oxidised by hydrogen peroxide in borate buffer; this oxidation reaction is significantly catalysed by trace amounts of Cu(II). Consequently, the main aim of this study was the development of a new sensitive kinetic-spectrophotometric method for the determination of Cu(II), based on its catalytic effect, and optimisation of the procedure for its simple and direct application in the presence of other species in real samples. Since this element is usually present at low levels in many environmental (natural and waste waters, soil and air), food, wines, drinks or biologically samples (blood, serum, urine), sensitive and selective analytical techniques are required for its determination. The developed kinetic procedure is sensitive, rapid, low-cost and applicable. The method was successfully applied to determination of traces amounts of Cu(II) in fruit, wine and milk samples. An ICP-OES method was also used for determination of Cu(II) in these samples, in order to validate the proposed kinetic-spectrophotometric method. The obtained results have shown good agreement. Also, based on the results of this work it can be seen that oxidation of Sunset Yellow, as widely used artificial dye for food and drinks, is catalysed by traces of metal ions, in presence of oxidative compounds (such as H_2O_2) in alkaline media, at about 25 °C, which is followed by decolourisation of such a kind of food and drink samples.

2. Materials and methods

2.1. Apparatus

Spectrophotometric measurements were performed on Perkin–Elmer Lambda 15 UV–vis spectrophotometer (Perkin–Elmer Instruments, Shelton, USA) using cylindrical cell thermostated at about 25.0 °C. For the pH measurements, Radiometer PHM 29Bb pH metre, (MeterLab, USA) and a combined glass–calomel electrode, GK2311C were used. All solutions were kept in a thermostatic water-bath at 25.0 ± 0.1 °C before the beginning of the reaction. ICP-OES measurements were done by means of an atomic-emission spectrometer SPECTRO CIROS^{CCD} (Spectro Analytical Instruments, Kleve, Germany). High precision measuring for laboratory applications was performed by using an analytical balance METTLER TOLEDO, AB204-S, Switzerland.

2.2. Reagents and solutions

Analytical grade chemicals and deionised water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions.

All the stock solutions were stored in polyethylene containers. All the polyethylene containers and the glassware used were cleaned in aqueous HCl (1:1) and then thoroughly rinsed with deionised water. A 1.000 g L^{-1} Cu(II) (nitrate salt, Merck®, KGaA, Darmstadt, Germany) was used as a stock solution. Cu(II) working solutions were made by suitable dilutions of the stock solution. A solution of SY (disodium-6-hydroxy-5-[(4-sulphophenyl)azo]-2-naphtalenesulphonic acid), Fluka (Bushs, Switzerland) of 1×10^{-3} mol L^{-1} was prepared by weighing 0.0226 g of substance of analytical grade, using an analytical balance, and dissolving with deionised water in a calibrated volumetric flask of 50 mL. A 2 mol L^{-1} solution of hydrogen peroxide (Merck®) was prepared by appropriate dilution of 30% of reagent in volumetric flask of 50 mL with deionised water. The solution of borate buffer was prepared by appropriate mixing a solution of $Na_2B_4O_7{\cdot}10H_2O$ (Merck®) of (0.05 mol L^{-1}) and 0.1 mol L^{-1} solution of NaOH. Sigma buffers, pH of 7.00 ± 0.01 and pH of 4.00 ± 0.01, were used to calibrate the pH metre.

2.3. Kinetic-spectrophotometric procedure

A suitable aliquot of Cu(II) solution, specified below for each sample, was transferred into a 10 mL standard flask with a glass stopper. Then, 0.2 mL of 10^{-3} mol L^{-1} solution of SY, and 2 mL borate buffer pH of 10.5 were added and the solution was diluted up to 4 mL with deionised water. The solution was kept at 25.0 ± 0.1 °C in the thermostated bath. After the temperature of the solution had reached 25.0 ± 0.1 °C, 1 mL of hydrogen peroxide solution of 2 mol L^{-1} was added in reaction mixture to initiate the reaction. The reaction mixture was transferred immediately into the spectrophotometric cell and the absorbance at 478.4 nm was measured every 30 s during the first period of 6 min from the beginning of the reaction. The method of tangents was used and the slope of the absorbance–time curve, $dA/dt = tg\alpha$, was used as a measure of the reaction rate.

2.4. ICP-OES conditions

The following ICP-OES conditions were applied: plasma power 1400 W, coolant flow 14.00 L/min, auxiliary flow 1.00 L/min and nebuliser flow 0.90 L/min. It is simultaneous spectrometer with radial viewed plasma, Paschen–Runge mount optical system and 22 linear CCDs placed detectors arranged on a Rowland's circle, enabling a spectral range 125–770 nm, and with a Scott-type spray chamber. Energy for the plasma was achieved with a free-running 27.12 MHz generator. Emission intensities were axially measured at 324.754 nm, as these conditions provided the highest sensitivity. Working parameters were controlled and altered using software package Smart Analyser Vision®. Calibration was performed using external standard prepared from 1000 g L^{-1} stock of Cu(II), made up as appropriate with 2% nitric acid.

2.5. Sampling plan and preparation of samples

The proposed kinetic method was applied for comparative determination of traces amounts of Cu(II) in samples of wine, grapes and milk, at different locations in South Serbia (Porecje, Vucje) and Kosovo (Mitrovica, Novo Brdo), in order to monitor the influence of different environmental and geo-morphological conditions on its contain in mentioned samples. The proposed kinetic method was also applied for determination of traces amounts of Cu(II) in fruit samples (lemon and orange – Tivat, Montenegro) and vineyard leaf.

The grape, wine (white, red) and milk samples (randomly selected, during 2007 autumn season) are collected at the same time from following area: (grape, red and white wine, vineyard leaf) – Porecje, Serbia; (red grape) – Mitrovica, Kosovo; (cow milk) – Porecje, Serbia and Novo Brdo, Kosovo; (lemon, orange) – Tivat, Montenegro. For the determination of trace levels of elements, contamination or loss are of prime consideration. Examined samples (lemon, orange and grape) are collected in plastic containers, and maintained at 4 °C during transport, protecting them from