

Determination of copper in tea leaves by flame atomic absorption spectrometry

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A simple method for the determination of Cu in different tea samples by flame atomic absorption spectrometry (FAAS) has been suggested. Optimal conditions of FAAS determination of copper were determined. Investigation of selectivity of the proposed FAAS method has shown that this procedure is not affected by high concentrations of other different metals. The FAAS method was applied to the determination of Cu in five different tea samples. The accuracy of the developed method was sufficient and proved by the method of addition. The results have demonstrated that the procedure can be applied for the analysis of tea samples with a satisfactory accuracy.

Key words: copper determination, tea samples, flame atomic absorption spectrometry, quantitative analysis

INTRODUCTION

At low concentrations, copper plays an important role in carbohydrate and lipid metabolism [1–3]. Above trace levels, however, copper has many biological effects both as an essential and a toxic element. For all trace elements that are considered to be essential, including copper, there exists a fairly narrow “concentration window” between the essential and the toxic levels. The metals can accumulate in bone, hair and in some soft tissues, such as liver, kidney, brain or lungs [4, 5]. Copper is a moderately toxic element as compared to other transition metals. However, the toxic doses of copper and its compounds can lead to serious problems. Severe oral intoxication will affect seriously the blood and kidneys [6]. Copper and its compounds have widespread industrial and domestic applications; hence, large quantities of copper are discharged into the environment. Therefore, trace copper content in water and food must be controlled on a daily basis.

Flame atomic absorption spectrometry (FAAS) is one of the techniques most extensively used for determining various elements with a significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operation cost. However, in some cases it is rather difficult to determine traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. Thus, a preconcentration and/or separation step is necessary [7–10]. For the de-

termination of different metals, including copper, by FAAS in different food and water samples, many methods such as extraction, coprecipitation, ion exchange and accumulation with a liquid membrane have been used for copper preconcentration [9, 11–15].

So far, very few precise and accurate methods for the determination of copper in tea leaves have been suggested. For example, differential pulse polarography preceded by solvent extraction of Cu(II) chelates in rather toxic chloroform was used for the determination of copper in tea specimens [16]. A copper(II) membrane coated graphite electrode based on Schiff's base and showing a very short lifetime was applied for the determination of copper in a sample of Iranian black tea [17]. Recently, the FAAS determination of trace copper in tea samples after preconcentration with 1-nitroso-2-naphthol-3,6-disulfonic acid on Ambersorb 572 has also been suggested [6]. However, this procedure was found to be very time-consuming. The aim of the present study was to propose a simple method for the determination of copper in different tea samples by FAAS without using any preconcentration procedure. The experimental conditions for the direct determination of copper were optimized.

EXPERIMENTAL

Double-distilled water and analytical-grade reagents were used in all the experiments. Stock standard solution of copper, 0.1 mg ml⁻¹, was prepared by dissolving an appropriate amount of metallic cop-

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per (99.99% purity) in diluted nitric acid (1:1). Copper ion standard solution was diluted daily for obtaining a working standard solution of copper ($100 \mu\text{g ml}^{-1}$). Standard solutions of other metals, $2 \cdot 10^4 \mu\text{g ml}^{-1}$, were prepared by dissolving appropriate amounts of: (i) metallic Cd, Co, Mn, Ni, and Pb in diluted nitric acid (1:1); (ii) metallic Al, Fe, and Mg or CaO and ZnO in diluted hydrochloric acid (1:1); (iii) metallic Cr in diluted sulfuric acid (1:4); (iv) metallic Bi in aqua regia; (v) salts BaCl_2 , KCl, Li_2SO_4 , NaCl, and $\text{Sr}(\text{NO}_3)_2$ in double-distilled water. Solutions of copper, $0.1 \mu\text{g ml}^{-1}$, along with appropriate amounts of interfering ions, were prepared for the evaluation of selectivity. Solution of copper of the same concentration without additives was used as a reference solution.

The calibration curve used for the determination of copper in tea samples by FAAS was established using the following procedure. An appropriate amount of working standard solution of copper and 5 ml of 2 M HCl were transferred to a 100-ml volumetric flask and diluted with double-distilled water. The calibration solutions were prepared over the concentration range $0.05\text{--}1.6 \mu\text{g ml}^{-1}$ Cu. For the determination of copper in tea leaves, 1 g of the oven-dried (105°C) sample was preheated for 0.5 h at 250°C and burned for 1 h at $800\text{--}850^\circ\text{C}$. The obtained ash was wetted with double-distilled water, mixed with 10 ml of diluted HCl (1:1), the mixture was mildly boiled, cooled to room temperature, filtered (if necessary), transferred to a 25-ml volumetric flask and diluted with double-distilled water.

A Hitachi 170-50 (Japan) flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the analysis. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Cu hollow cathode lamp operating at 324.8 nm was used as the radiation source. The lamp current was set at 10 mA. The flame composition was a mixture of propane-butane (gas pressure $9.81 \cdot 10^5$ Pa) and air (gas pressure $1.47 \cdot 10^7$ Pa).

RESULTS AND DISCUSSION

The analytical features of the developed procedure were found to be comparable to those reported in previous papers for copper determination in environmental samples. For example, the absorbance of copper solutions showed no difference for approximately three months. The influence of different inorganic acids (HCl , HNO_3 , and H_2SO_4) used in the analytical procedure on the absorbance of copper was also estimated. The nature of acid showed no significant influence on the analytical signal. The dependence of the absorbance of copper on the propane-butane gas

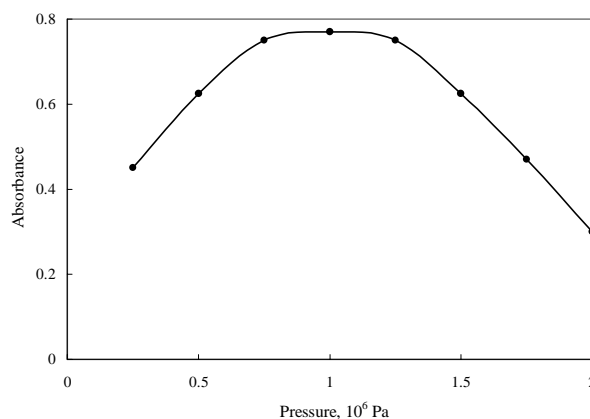


Fig. 1. Dependence of copper absorbance on propane-butane gas pressure. Air gas pressure = $1.47 \cdot 10^7$ Pa; $c_{\text{Cu}} = 0.5 \mu\text{g ml}^{-1}$

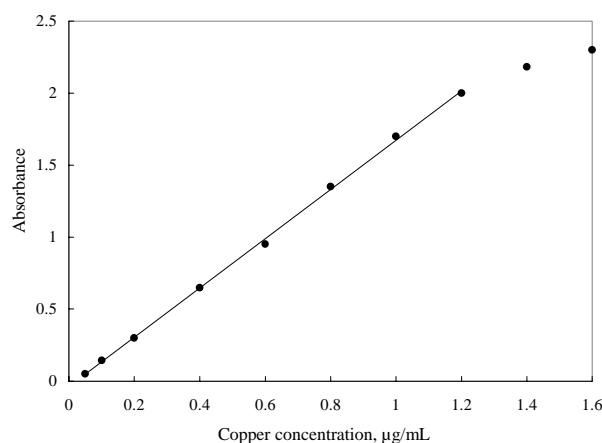


Fig. 2. Correlation between absorbance and copper concentration

pressure used for the atomization of copper is shown in Fig. 1. One can see that the absorbance of copper is stable in the range of gas pressure from $7.5 \cdot 10^5$ to $12.5 \cdot 10^5$ Pa. The calibration curve obtained under the best conditions showed a linear correlation within the concentration range from $0.05\text{--}1.2 \mu\text{g ml}^{-1}$ (Fig. 2).

An attempt was also made to examine the effects of representative potential interfering species on the determination of copper with FAAS. In order to determine the selectivity of the method, solutions containing copper and other metal ions were prepared and analyzed. The Cu/M interfering ratios were considered as limiting when the error of the determination did not exceed $\pm 10\%$ [7]. The selectivity studies are summarized in Figs. 3-6.

Evidently, the least influence on the absorbance of copper is shown by Na, K, Ca, Mg, Co and Cd (Fig. 3). These metals did not show any interference in copper determination by FAAS, even if their concentrations were 20,000 times higher than those of Cu. A stronger influence on the determination

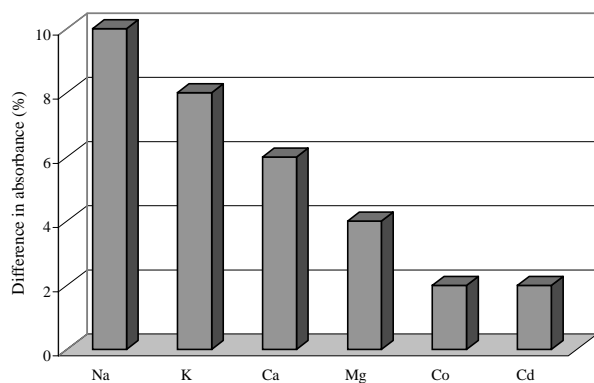


Fig. 3. Effect of the concentration of Na, K, Ca, Mg, Co, and Cd ions on the analytical signal of Cu (Cu: M = 1: 20 000)

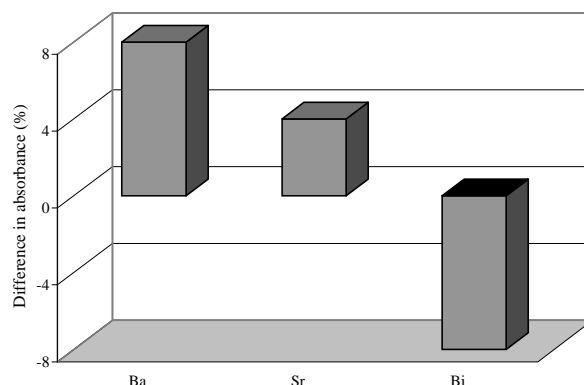


Fig. 5. Effect of the concentration of Ba, Sr, and Bi ions on the analytical signal of Cu (Cu: M = 1: 6 000)

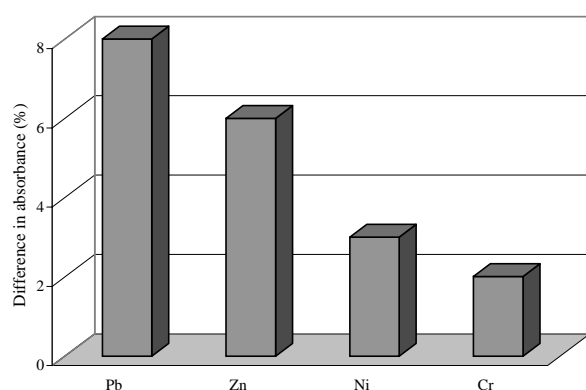


Fig. 4. Effect of the concentration of Pb, Zn, Ni, and Cr ions on the analytical signal of Cu (Cu: M = 1: 12 000)

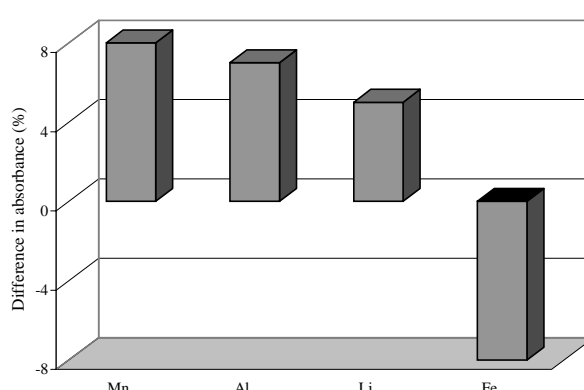


Fig. 6. Effect of the concentration of Mn, Al, Li, and Fe ions on the analytical signal of Cu (Cu: M = 1: 2 000)

Table. Results obtained for the determination of copper in tea samples (n = 5, P = 0.95)

Tea sample	Cu found by FAAS method (mg kg ⁻¹)	S _r (%)	Added amount of Cu (mg kg ⁻¹)	Total amount of Cu found by FAAS method (mg kg ⁻¹)	Recovery (%)
<i>Brooke Bond</i>	33.9	2.9	20	53.4	99
<i>Georgian</i>	23.3	2.8	20	43.3	100
<i>Dilmah</i>	32.9	1.2	20	53.4	101
<i>Ceylon</i>	28.9	2.0	20	48.4	99
<i>Chinese green</i>	19.8	1.6	20	40.6	102

of copper was observed for Pb, Zn, Ni and Cr (see Fig. 4). These metals did not show any interference in copper determination by FAAS if their concentrations were 12,000 times higher than that of Cu. A twice as high influence on the determination of copper was observed for Ba, Sr and Bi (see Fig. 5). Figure 6 implies that Mn, Al, Li and Fe have the highest interfering effects on copper determination. These metals could be tolerated up to their concentrations at least 2000 times higher than those of Cu. Therefore, according to the interfering effect the examined metals can be ordered as Mn, Al, Li, Fe > Ba, Sr, Bi > Pb, Zn, Ni, Cr > Na, K, Ca, Mg, Co, Cd. Moreover, these results clearly indicate the high level of selectivity of the FAAS method,

and no masking reagents are required for the efficient determination of copper in tea samples.

Determination of copper was performed in several commercially available tea samples, such as *Brooke Bond*, *Georgian*, *Dilmah*, *Ceylon* and *Chinese green* tea leaves. The accuracy of the results of analytical determination of copper was evaluated by the method of addition. The results obtained for copper determination by the FAAS method are summarized in Table. The concentration of Cu in tea leaves ranged from 33.9 mg kg⁻¹ (*Brooke Bond*) to 19.8 mg kg⁻¹ (*Chinese green*). Besides, the results in Table confirm that the accuracy of the developed flame atomic absorption spectrometric method of the determination of Cu in tea samples is efficient.

Moreover, the proposed analytical procedure is simple, fast, selective and not labor-intensive.

CONCLUSIONS

The main characteristics for the determination of copper in tea leaves by FAAS have been investigated. It has been demonstrated that the nature of inorganic acid does not exert a significant influence on the absorbance of copper. However, the analytical signal was found to be dependent very much on the propane-butane gas pressure used for the atomization of copper. The absorbance of copper was stable only in a rather narrow range of gas pressure (from $7.5 \cdot 10^5$ to $12.5 \cdot 10^5$ Pa). The calibration curve obtained under the best conditions showed a linear correlation within the concentration range from 0.05–1.2 $\mu\text{g ml}^{-1}$. The observed detection limit of copper is about 0.05 $\mu\text{g ml}^{-1}$. According to the interfering effect, the examined metals can be ordered as Mn, Al, Li, Fe > Ba, Sr, Bi > Pb, Zn, Ni, Cr > Na, K, Ca, Mg, Co, Cd. A method for the direct determination of copper in different tea samples by FAAS has been developed. The methodology showed an excellent reproducibility and accuracy. In addition, the proposed method shows a low analytical cost, fairly easy operation, simplicity and needs short time for analysis.

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References

1. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, New York, (1984).
2. E. M. de Moraes Flores, A. B. da Costa, J. S. Barin, V. L. Dressler, J. N. G. Paniz and A. F. Martins, *Spectrochimica Acta Part B: Atomic Spectr.*, **56**, 1875 (2001).
3. E. M. de Moraes Flores, A. P. F. Saidelles, E. L. de Moraes Flores, M. F. Mesko, M. P. Pedroso, V. L. Dressler, C. L. Bittencourt and A. B. da Costa, *Microchem. J.*, **77**, 113 (2004).
4. R. Prego and A. Cobelo-Garcia, *Env. Poll.*, **121**, 425 (2003).
5. J. L. Manzoori and A. Bavili-Tabrizi, *Anal. Chim. Acta*, **470**, 215 (2002).
6. E. Kenduzler and A. R. Turker, *Anal. Chim. Acta*, **480**, 259 (2003).
7. V. Viëkaëkaitë, S. Tautkus and R. Kazlauskas, *Chem. Anal. (Warsaw)*, **41**, 483 (1996).
8. S. L. C. Ferreira, W. N. L. dos Santos and V. A. Lemos, *Anal. Chim. Acta*, **445**, 145 (2001).
9. A. N. Anthemidis, G. A. Zachariadis and J. A. Stratis, *Talanta*, **58**, 831 (2002).
10. S. Tautkus, L. Steponieniene and R. Kazlauskas, *J. Serb. Chem. Soc.*, **69**, 393 (2004).
11. A. N. Anthemidis, G. A. Zachariadis and J. A. Stratis, *Talanta*, **54**, 935 (2001).
12. V. A. Lemos, P. X. Baliza, R. T. Yamaki, M. E. Rocha and A. P. O. Alves, *Talanta*, **61**, 675 (2003).
13. S. L. C. Ferreira, M. A. Bezerra, W. N. L. dos Santos and B. B. Neto, *Talanta*, **61**, 295 (2003).
14. E. L. da Silva, A. M. Martins, A. Valentini, V. T. de Favere and E. Carasek, *Talanta*, **64**, 181 (2004).
15. C. Mendiguchia, C. Moreno and M. Garcia-Vargas, *Anal. Chim. Acta*, **460**, 35 (2002).
16. M. H. Pournaghi-Azar and F. Farajnia, *Microchem. J.*, **63**, 285 (1999).
17. M. R. Ganjali, T. Poursaberi, L. H. Babaei, S. Rouhani, M. Yousefi, M. Kargar-Razi, A. Moghimi, H. Aghabozorg, M. Shamsipur, *Anal. Chim. Acta*, **440**, 81 (2001).

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VARIO NUSTATYMAS ARBATPOLËSE ATOMINËS ABSORBCINËS SPEKTROMETRIJOS METODU

Santrauka

Iðtirtos ir optimizuotos pagrindinës vario nustatymo sàlygos liepsnos atominës absorbcinës spektrometrijos (FAAS) metodu ir parengta efektyvi metodika variui nustatyti arbatpolëse. Nustatyta, kad absorbcijos signalas tiesiškai priklauso nuo vario koncentracijos intervale 0,05–1,2 $\mu\text{g ml}^{-1}$, kai propano–butano dujø slëgis iðlieka $7,5 \cdot 10^5$ – $12,5 \cdot 10^5$ Pa. Maþiausia vario nustatymo riba – 0,05 $\mu\text{g ml}^{-1}$. Optimizuotos metodikos atrankumo tyrimo rezultatai parodë, kad maþiausia àtakà vario atominei absorbcijai turi Na, K, Ca, Mg, Co ir Cd. Jie netrukdo nustatyti varà, net kai jø koncentracijos 20000 kartø didesnës uþ vario koncentracijos tiriamojame sistemoje. 12000 kartø didesnës Pb, Zn, Ni ir Cr koncentracijos taip pat neturi àtakos vario atominei absorbcijai. Nustatyta, kad Ba, Sr ir Bi koncentracijos gali bûti didesnës uþ vario koncentracijà apie 6000 kartø. Ðiek tiek didesnë àtakà turi Mn, Al, Li ir Fe – jie netrukdo nustatyti varà, kai jø koncentracijos 2000 kartø didesnës uþ vario koncentracijà tirpale. Parengta ir pritaikyta variui nustatyti arbatpolëse FAAS metodika yra tiksli, paprasta, greita, ekonomiðka, pasiþymi aukøtu atrankumu ir gali bûti sëkmingai taikoma efektyviai vario kiekio kontrolei ðiuose maisto produktuose.