

DETERMINATION OF COPPER AT WIDE RANGE CONCENTRATIONS USING INSTRUMENTAL FEATURES OF HIGH-RESOLUTION CONTINUUM SOURCE FLAME ATOMIC ABSORPTION SPECTROMETRY

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Abstract: This work describes a method to determine Cu at wide range concentrations in a single run without need of further dilutions employing high-resolution continuum source flame atomic absorption spectrometry. Different atomic lines for Cu at 324.754 nm, 327.396 nm, 222.570 nm, 249.215 nm and 224.426 nm were evaluated and main figures of merit established. Absorbance measurements at 324.754 nm, 249.215 nm and 224.426 nm allows the determination of Cu in the 0.07 – 5.0 mg L⁻¹, 5.0 – 100 mg L⁻¹ and 100 – 800 mg L⁻¹ concentration intervals respectively with linear correlation coefficients better than 0.998. Limits of detection were 21 µg L⁻¹, 310 µg L⁻¹ and 1400 µg L⁻¹ for 324.754 nm, 249.215 nm and 224.426 nm, respectively and relative standard deviations ($n = 12$) were $\leq 2.7\%$. The proposed method was applied to water samples spiked with Cu and the results were in agreement at a 95% of confidence level (paired *t*-test) with those obtained by line-source flame atomic absorption spectrometry.

Keywords: Copper, HR-CS FAAS, Wide range determination,

Introduction

Copper is usually present at different concentration levels in a variety of workable samples [1]. The elemental determination by atomic absorption spectrometry [2,3] is frequently performed by line source spectrometers. Although the line-source flame atomic absorption spectrometry (LS FAAS) [4] is a worldwide, robust and well-established technique, the single-element analysis and narrow range calibration may be considered the main drawbacks of the technique when several elements are required: the changing and conditioning of hollow cathode lamps (or electrodeless discharge lamps) and the need for adjusting analyte absorbance within the linear working range of calibrating plots are time consuming and lead to increased analytical

cost in large scale routine analyses [5]. However, these cumbersome may be circumvented using a high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS). With this new concept, a high-resolution double-Echelle monochromator and a charge-couple device detector with a xenon arc-short lamp with a continuum source [6] makes feasible the application of the atomic absorption spectrometry for fast-sequential and multi-element analyses [7] using one or more atomic lines of the same element sequentially, wavelength-integrated absorbance over the line core to enhance sensitivity, or at least measuring parts of the wings (side pixel registration) to extend the linear working range calibration [8-10]. The fast-sequential analysis is a particularly advantageous for routine laboratories involved in large scale analyses, because time and

analytical costs are significantly reduced. Little attention has been given to the use secondary and alternating lines in flame AAS to reduce sensitivity and increase the dynamic working range to determine low, intermediate and high levels of an element in a single run without need of further dilutions.

In this work the main (324.754 nm), secondary (327.396 nm) and alternate (222.570 nm, 249.215 nm and 224.426 nm) lines of Cu were evaluated in order to develop a method for wide range determination using instrumental facilities of the HR-CS FAAS.

Experimental

Instrumentation

The measurements were carried out using an Analytik Jena ContrAA 300 high-resolution continuum source flame atomic absorption spectrometer equipped with a xenon short-arc lamp XBO 301 (GLE, Berlin, Germany) [11] with a nominal power of 300 W operating in a hot-spot mode as a continuum radiation source. Main (324.754 nm), secondary (327.396 nm) and alternate (222.570 nm, 249.215 nm and 224.426 nm) atomic lines for Cu were evaluated to establish the figures of merit of all lines. High-purity acetylene (99.7%, Air Liquid, Sertãozinho, Brazil) was used as fuel gas, and an oxidizing air-acetylene flame was used for analyte atomization. A Perkin Elmer Analyst 100 line source spectrometer (Shelton, CT, USA) was also used as comparative technique, and the determination of Cu was carried out in an air-acetylene flame using a Perkin-Elmer Lumina™ hollow cathode lamp.

Reagents, analytical solutions and samples

High-purity de-ionized water obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q Academic® deionizer system (resistivity 18.2 MΩ cm, Millipore, Bedford, MA, USA), and nitric acid (Suprapur®, Merck, Germany) were used throughout to prepare all solutions.

A 5000 mg L⁻¹ Cu standard stock solution was prepared by dissolving 1.0 g of metallic copper (99.9% purity) in a minimum volume of concentrated nitric acid. The final solution was transferred to a 200 mL volumetric flask and the volume completed with 1.0% (v/v) HNO₃ solution.

Copper working standard solutions in the 0.05 – 1000 mg L⁻¹ interval were prepared by appropriate dilution of the stock standard solutions

and acidified to 1.0% (v/v) with HNO₃. For LS FAAS the concentration interval was 0.5 – 5.0 mg L⁻¹.

Tap water samples spiked with Cu within 1.0 – 600 mg L⁻¹ were used to check the accuracy and the effectiveness of the proposed method.

All solutions and samples were stored in high-density polypropylene bottles (Nalgene®, Rochester, USA). Plastic bottles and glassware materials were cleaned by soaking in 10% (v/v) HNO₃ at least 24 h and rinsed abundantly in de-ionized water before use.

Measurement procedure

Absorbance measurements were carried out at 324.754 nm, 327.396 nm, 222.570 nm, 249.215 nm, and 224.426 nm. The equipment was optimized to provide the best sensitivity. For wavelength-integrated absorbance equivalent to 3 pixels, 5.0 mL min⁻¹ of sample flow-rate, the absorbance for blanks, working standard solution and spiked samples solutions were measured at the selected atomic lines for Cu to obtain the calibration curves for all wavelengths. All measurements were carried out in six replicates using an injection module (SFS 6) enabling the computer controlled aspiration of blanks, working standard solutions and samples.

All samples were also analyzed by LS FAAS at the main line of Cu at 324.754 nm. Because the instrumental limitations of technique, spiked samples were diluted to adjust the analyte absorbance within the linear working range. All measurements were carried out in triplicate.

The limit of detection (LOD) and limit of quantification (LOQ) for Cu were calculated according to the IUPAC recommendation [12].

Results and discussion

In HR-CS FAAS the continuum radiation source provides a better SNR than hollow cathode lamps usually found in LS FAAS. In this context, the use of secondary and alternate atomic lines of a given element is a good strategy to reduce sensitivity and extend the working range calibration.

Optimization of the best condition for different wavelengths for Cu

The performance of atomic lines for Cu at 324.754 nm, 327.396 nm, 222.570 nm, 249.215 nm

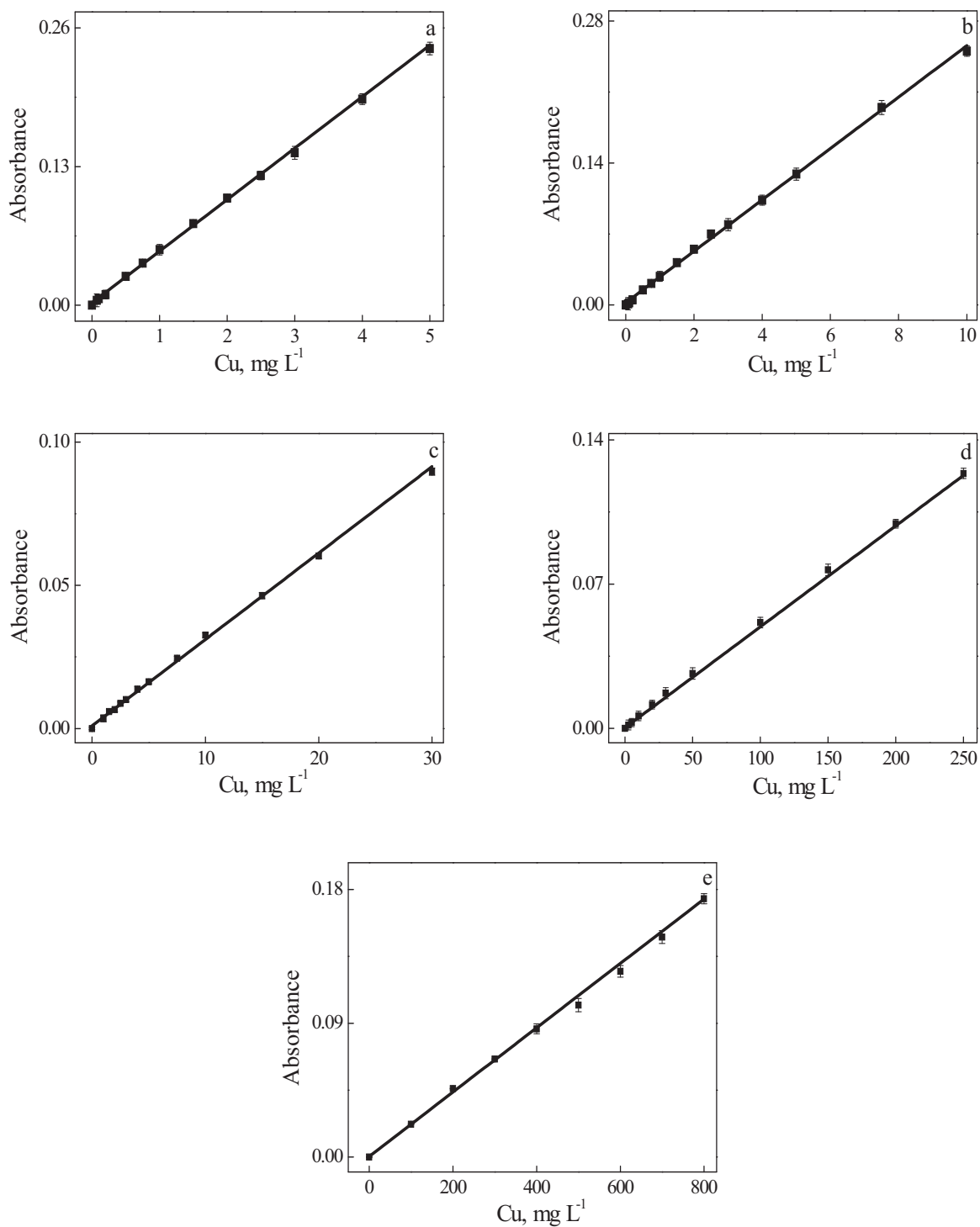


Figure 1. Calibration plots for Cu at 324.754 nm (a), 327.396 nm (b), 222.570 nm (c), 249.215 nm (d) and 224.426 nm (e) built up by using HR-CS FAAS.

and 224.426 nm was checked after evaluating the burner height and flame composition. Absorbance is affected by alterations in the flame composition due to changes on the temperature and atomization degrees, and by adjustment of burner height to obtain the best optical axis for the light path of the xenon short-arc lamp [6]. The influence of variation of the burner height (4 – 5 – 6 – 7 – 8 mm) and the ratio of air-acetylene flow rates (0.088 – 0.098 – 0.108 – 0.118 – 0.128) on absorbance of Cu were evaluated using 0.5 mg L⁻¹ (324.754 nm), 1.0 mg L⁻¹ (327.396 nm), 4.0 mg L⁻¹ (222.570 nm), 50 mg L⁻¹ (249.215 nm) and 200 mg L⁻¹ (224.426 nm) concentrations. Different fuel-oxidant ratios were obtained by changing the flow rate of acetylene at 45, 50, 55, 60 and 65 L h⁻¹ and keeping fixed the air flow-rate at 508 L h⁻¹. The best situations achieved for burner height and flame composition for each wavelength studied were 4 mm and 65 L h⁻¹ (324.754 nm), 4 mm and 55 L h⁻¹ (327.396 nm), 4 mm and 40 L h⁻¹ (222.570 nm), 7 mm and 80 L h⁻¹ (249.215 nm) and 7 mm and 50 L h⁻¹ (224.426 nm), respectively.

After burner height and flame composition optimization, the linear working range was evaluated by plotting curves of absorbance *versus* analyte concentration within the 0.05 – 1000 mg L⁻¹ intervals (Figure 1). Analysis of figure reveals that calibration curves in the 0.07 – 5.0 mg L⁻¹ (324.754 nm), 0.07 – 10.0 mg L⁻¹ (327.396 nm), 1.0 – 30.0 mg L⁻¹ (222.570 nm), 5.0 – 100 mg L⁻¹ (249.215 nm) and 100 – 800 mg L⁻¹ (224.426 nm) intervals with typical linear

correlation coefficients better than 0.998 can be built up. The main figures of merit of studied atomic lines by HR-CS FAAS and LS-FAAS are shown in Table 1. Analysis of this table reveals that the highest sensitivity (0.0718 A.L mg⁻¹) was attained with the main line at 324.754 nm by HR-CS FAAS, followed by the same wavelength by LS AAS. For both techniques the upper limit linear response was 5.0 mg L⁻¹. For this wavelength, the LOD calculated for HR-CS FAAS (21 mg L⁻¹) was better than that calculated for LS AAS (45 mg L⁻¹). This may be attributed to the higher intensity of the xenon arc lamp in comparison to Cu hollow cathode lamp. The use of the secondary line 327.396 nm allowed extending the calibration up to 10.0 mg L⁻¹. The wavelengths 222.570 nm, 249.215 nm and 224.426 nm allowed extending the calibration up to 30.0 mg L⁻¹, 100 mg L⁻¹ and 800 mg L⁻¹, respectively. It is interesting to note that the characteristic concentration and LOD increases in the following order 324.754 nm, 327.396 nm, 222.570 nm, 249.215 nm, and 224.426 nm. The correlation coefficients of all curves were always better than 0.998. The relative standard deviation (r.s.d.) varied from 1.2% (324.754 nm) to 2.7% (224.426 nm), suggesting all lines give precise measurements. Analysis of Table 1 reveals that 3 distinct calibration curves cover the fast-sequential determination of Cu within the 0.07 – 800 mg L⁻¹ concentration range using only 3 wavelengths: 324.754 nm (0.07 – 5.0 mg L⁻¹), 249.215 nm (5.0 – 100 mg L⁻¹), and 224.426 nm (100 – 800 mg L⁻¹).

Table 1. Figures of merit of main (324.754 nm), secondary (327.396 nm) and alternate (222.570 nm, 249.215 nm and 224.426 nm) atomic lines for Cu by HR-CS FAAS and for 324.754 nm by LS-FAAS.

Wavelength (nm)	Technique	Calibration (mg L ⁻¹)	Slope (A.L.mg ⁻¹)	R ^a	C ₀ ^b (mg L ⁻¹)	LOD ^c (µg L ⁻¹)	r.s.d. (%)
324.754	LS FAAS	0.5 – 5.0	0.0507	0.9996	0.24	45	2.0
324.754	CS FAAS	0.1 – 5.0	0.0718	0.9991	0.11	21	1.2
327.396	CS FAAS	0.07 – 10.0	0.0254	0.9985	0.17	47	1.7
222.570	CS FAAS	1.0 – 30.0	0.0030	0.9981	1.5	114	1.8
249.215	CS FAAS	5.0 – 100	0.0005	0.9990	8.8	310	2.2
224.426	CS FAAS	100 – 800	0.0002	0.9995	22	1410	2.7

^aLinear correlation coefficient

^bCharacteristic concentration

^cLimit of detection

Table 2. Results for spiked Cu (mean \pm standard deviation) determined ($n = 3$) in tap water samples by HR-CS FAAS by the proposed method and by LS-FAAS.

Sample	Spike, mg L ⁻¹	Found, mg L ⁻¹				Recovery, %	
		324.754 nm		249.215 nm			
		LS*	CS	LS	CS		
1	1.00	1.03 \pm 0.04	1.01 \pm 0.02	---	---	103	101
	2.00	1.96 \pm 0.06	1.98 \pm 0.03	---	---	98	99
	4.00	4.08 \pm 0.09	4.04 \pm 0.05	---	---	102	101
2*	20.0	20.8 \pm 0.7	---	20.6 \pm 0.5	---	104	103
	40.0	39.1 \pm 1.1	---	39.5 \pm 0.7	---	98	99
	80.0	82.2 \pm 2.5	---	81.0 \pm 1.3	---	103	101
3*	200	204 \pm 6	---	---	202 \pm 3	102	101
	400	412 \pm 14	---	---	408 \pm 7	103	102
	600	615 \pm 17	---	---	607 \pm 11	103	102

*samples diluted to adjust the analyte absorbance within the linear working range calibration for LS-FAAS

Analyses of real samples

After method development, three analytical curves in the 0.07 – 800 mg L⁻¹ Cu concentration range were always obtained to determine Cu in three tap water samples spiked with 1.0 – 2.0 – 4.0 – 20 – 40 – 80 – 200 – 400 – 600 mg L⁻¹ Cu using the atomic lines 324.754 nm, 249.215 nm and 224.426 nm. Table 2 shown results found by HR-CS FAAS using the proposed method. Results described in the table are in agreement at 95% of confidence level (paired *t*-test) with those obtained by LS-FAAS. Accuracy studies were carried out by recoveries tests and the results obtained by HR-CS FAAS varied within the 98 - 103% and for LS FAAS within the 97 - 104% intervals. Relative standard deviations for the measurements ($n = 12$) varied from 1.2% to 2.0% (324.754 nm), from 1.6% to 2.6% (249.215 nm) and from 1.5% to 1.8% (224.426 nm) by HR-CS FAAS and from 2.2% to 3.9% by LS FAAS. Limits of detection calculated for HR-CS FAAS were 21 μ g L⁻¹

(324.754 nm); 300 μ g L⁻¹ (249.215 nm) and 1410 μ g L⁻¹ (224.426 nm).

Conclusions

The use of different atomic lines of a given element in HR-CS FAAS is feasible to elemental determination in a wide range concentration without need of further dilutions of samples, reducing the errors associated to the excessive sample handling. The example here is the determination of low, medium and high concentrations of Cu in waters, but can be extended to other element and matrix.

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Resumo: Este trabalho descreve um método de determinação de cobre por espectrometria de absorção atômica em chama com fonte contínua e alta resolução em amplo intervalo de concentração sem necessidade de diluições sucessivas. Diferentes linhas atômicas foram avaliadas (324,754 - 327,396 - 222,570 - 249,215 - 224,426 nm) e as suas principais figuras de mérito foram estabelecidas. Medidas de absorbância nas linhas 324,754 nm, 249,215 nm e 224,426 nm viabilizou determinar Cu nos intervalos de concentração 0,07 – 5,0 mg L⁻¹, 5,0 – 100 mg L⁻¹ e 100 – 800 mg L⁻¹ respectivamente com coeficientes de correlação lineares r^2 0.998. Os limites de detecção foram 21 µg L⁻¹, 310 µg L⁻¹ e 1400 µg L⁻¹ para 324,754 nm, 249,215 nm e 224,426 nm, respectivamente, e os desvios padrão relativos ($n = 12$) foram $\leq 2.7\%$. O método proposto foi aplicado na análise de águas adicionadas do analito e os resultados foram concordantes ao nível de 95% de confiança (teste *t*-pareado) com os obtidos por espectrometria de absorção atômica em chama com fonte de linhas.

Palavras-chave: Cobre, HR-CS FAAS, Amplo intervalo de determinação.

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