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Analytical Methodology for Determination of Trace Cu in Hydrated Alcohol Fuel

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1. Introduction

Many private and governmental initiatives have been established worldwide to identify viable alternatives to petroleum derivatives [1,2]. The goals are to reduce dependence on imported energy from non-renewable sources, while mitigating environmental problems caused by petroleum products, and to develop national technologies in the alternative energy field.

Ethyl alcohol (ethanol) is considered to be a highly viable alternative fuel. Its production from biomass means that it can provide a source of energy that is both clean and renewable. The inclusion of ethanol as a component of gasoline can help to reduce problems of pollution in many regions, since it eliminates the need to use tetraethyl lead (historically notorious as a highly toxic trace component of the atmosphere in major cities) as an anti-knock additive.

The quantitative monitoring of metal elements in fuels (including gasoline, alcohol, and diesel) is important from an economic perspective in the fuel industry as well as in the areas of transport and environment. The presence of metal species (ions or organometallic compounds) in automotive fuels can cause engine corrosion, reduce performance, and contribute to environmental contamination [2-5].

The low concentrations of metals in fuels typically require the use of sensitive spectrometric analytical techniques for the purposes of quality control. Atomic absorption spectrometry (AAS) can be applied for the quantitative determination of many elements (metals and semi-metals) in a wide variety of media including fuels, foodstuffs, and biological, environmental, and geological materials, amongst others. The principle of the technique is based on measurement of the absorption of optical radiation, emitted from a source, by ground-state atoms in the gas phase. Atomization can be achieved using a flame, electrothermal heating, or specific chemical

reaction (such as the generation of Hg cold vapor). Electrothermalatomizers include graphite tubes, tungsten filaments, and quartz tubes (for atomization of hydrides), as well as metal or ceramic tubes. Flame atomic absorption spectrometry (FAAS) is mostly used for elemental analysis at higher concentration levels, of the order of mg L⁻¹[3-5]. Table 1 lists some of the published studies concerning the application of AAS for determination of metals in fuels.

Technique	Matrix	Sample preparation	Reference
Graphite furnace atomic absorption spectrometry (GFAAS)	Fuel oil	Microwave digestion	6
Flame atomic absorption spectrometry	Fuel oil	Wet digestion	7
Atomic fluorescence spectrometry with cold vapor generation	Gasoline and other petroleum derivatives	Wet digestion	8
Graphite furnace atomic absorption spectrometry	Fuel oil	Microwave digestion	9
Graphite furnace atomic absorption spectrometry	Crude fuel oil	Dilution in xylene/I ₂ , wet and microwave digestion	10
Flame atomic absorption spectrometry	Engine oil	Wet digestion	11
Graphite furnace atomic absorption spectrometry	Fuel oils and naphtha	Oil-water emulsion	12
Inductively coupled plasma mass spectrometry (ICP-MS)	Gasoline	Emulsion with Triton X-100 surfactant	13
Flame atomic absorption spectrometry	Ethyl alcohol	Dilution in HNO ₃	5
Graphite furnace atomic absorption spectrometry	Ethyl alcohol	Dilution in HNO ₃	3,4
Graphite furnace atomic absorption spectrometry	Ethyl alcohol	Dilution in HNO ₃	2
Graphite furnace atomic absorption spectrometry	Ethyl alcohol and acids	Dilution in HNO ₃	14
Graphite furnace atomic absorption spectrometry with a high-resolution continuum source (HR-CS-GFAAS)	Crude oil	Oil-water emulsion	15
Atomic absorption spectrometry with thermal nebulization in a tube heated in a flame (TS-FF-AAS)	Ethyl alcohol fuel and gasoline	Dilution in HNO ₃ /oil-water emulsion	16
Graphite furnace atomic absorption spectrometry with a high-resolution continuum source	Crude oil	Oil-water emulsion	17

Technique	Matrix	Sample preparation	Reference
Atomic absorption spectrometry	Gasoline, diesel, ethyl alcohol and biodiesel	- (Review)	18
Graphite furnace atomic absorption spectrometry	Ethyl alcohol and acids	Direct determination	19
Graphite furnace atomic absorption spectrometry	Biodiesel	Microwave digestion and emulsion	1
Flame atomic absorption spectrometry	Ethyl alcohol	Solid phase extraction	20
Graphite furnace atomic absorption spectrometry	Biodiesel	Emulsion	21
Atomic absorption spectrometry with vapor generation (VP-FAAS)	Ethyl alcohol	Treatment with acid under UV irradiation	22

Table 1. Analytical methods for the determination of inorganic contaminants in fuels.

The thermospray (TS) technique was originally developed by Vestal et al. in 1978 [23] as an interface between liquid chromatography and mass spectrometry. In atomic absorption spectrometry, the tube was heated electrically in order to maintain a constant temperature, which restricted use of the method to only a few elements. However, Gáspár and Berndt (2000) proposed the TS-FF-AAS procedure, in which a metal tube is positioned above the flame of the atomic absorption spectrometer, as a reactor. The sample solution is transported through a metal capillary, connected to the tube, and heated simultaneously by the flame. On reaching the hot tip of the capillary, the liquid partially vaporizes, forming an aerosol. In turn, the aerosol is vaporized within the tube, producing an atomic cloud that absorbs the radiation emitted by the lamp.

The TS-FF-AAS method was used as an interface between high performance liquid chromatography (HPLC) and FAAS, employing a flow injection system [25-60].

The objective of this work is to describe the analysis of Cu present in hydrated ethyl alcohol fuel (HEAF) using the technique of atomic absorption spectrometry with thermal nebulization in a tube heated in a flame (TS-FF-AAS). The atomizers used were a metal tube (Ni-Cr alloy) and a ceramic tube (Al_2O_3).

2. Experimental procedures

2.1. Instruments and accessories

The instrumentation consisted of an atomic absorption spectrometer fitted with a flame atomizer (Perkin-Elmer, model AAnalyst 100), a hollow cathode Cu lamp ($\lambda = 324.8$ nm, slit width = 0.7 nm, $i = 15$ mA), with an air/acetylene (4:2 ratio) flame gas mixture, and back-

ground correction using a deuterium lamp. Other equipment comprised an analytical balance (Sartorius BL 2105) and a peristaltic pump (Ismatec, model ICP 8).

The TS-FF-AAS assembly employed a Rheodyne RE9725 injection valve, PEEK tubing, and a ceramic thermocouple insulator capillary (OMEGATITE450, OMEGA, USA). The capillary was composed of Al_2O_3 (>99.8%), resistant to temperatures up to 1900 °C, with $\varnothing_{\text{ext}} = 1.6$ mm and two orifices with $\varnothing_{\text{int}} = 0.4$ mm (this capillary provided better results than a stainless steel HPLC capillary, with less noise in the absorbance signal). The atomization tubes were a metal tube composed of Ni-Cr super-alloy (Inconel, length 100 mm, $\varnothing_{\text{int}} = 10.0$ mm, $\varnothing_{\text{ext}} = 12.0$ mm, 6 orifices with $\varnothing = 2.5$ mm, perpendicular to an orifice with $\varnothing = 2.0$ mm), and a ceramic tube (99.9% Al_2O_3 , length 100 mm, $\varnothing_{\text{int}} = 10.0$ mm, $\varnothing_{\text{ext}} = 12.0$ mm, 6 orifices with $\varnothing = 2.5$ mm, perpendicular to an orifice with $\varnothing = 2.0$ mm).

Data acquisition employed the software MQDOS (Microquímica), and the absorbance values were proportional to the height of the transient signals.

The temperature in the interior of the atomization tube was measured in two ways. The first method employed a thermocouple with an earthed connection, positioned adjacent to the metal tube, oriented towards the orifice where the ceramic capillary used to introduce the sample into the atomizer was located. The temperature measured for the metal tube was $983 \pm 1^\circ\text{C}$. Secondly, the thermocouple with connection exposed was positioned adjacent to the ceramic capillary within the tube, where a temperature of between 1030 °C and 1060°C was measured, at which the tube glowed ruby-red above the flame [16,40,45,54].

When 50 μL of HNO_3 (~ 0.1 mol L^{-1}) was injected at a rate of approximately 1.5 mL min^{-1} , there was a temperature reduction of around 50°C, due to cooling of the tube by the solution, followed by a rapid return to the maximum temperature range.

2.2. Reagents, solutions and samples

Working standard solutions were prepared from a stock 1000 mg L^{-1} copper standard solution (spectroscopic grade), by dilution in 0.14 mol L^{-1} HNO_3 (Synth).

The HEAF samples were prepared by mixing the fuel with an equal volume of 0.14 mol L^{-1} HNO_3 , with final volumes of 50 mL [3-5]. Subsequent quantification employed the standard additions procedure.

2.3. Assembly of the TS-FF-AAS system

A schematic diagram of the TS-FF-AAS system is shown in Figure 1.

It is recommended that the Inconel tube should only be positioned above the burner head after lighting the flame, to avoid the possibility of an explosion within the tube due to gas accumulation. The TS-FF-AAS system was therefore first assembled, after which the spectrometer flame was ignited immediately after opening the gas valves to avoid any explosion risk. This procedure facilitated the positioning of the tube above the burner head, which was performed while the flame was extinguished. All analyses employed a fixed volume of sam-

ple, injected into the flow of air as the carrier, since previous work has shown that injection using carrier solutions results in greater sample dilution and dispersion [40,45,54,58].

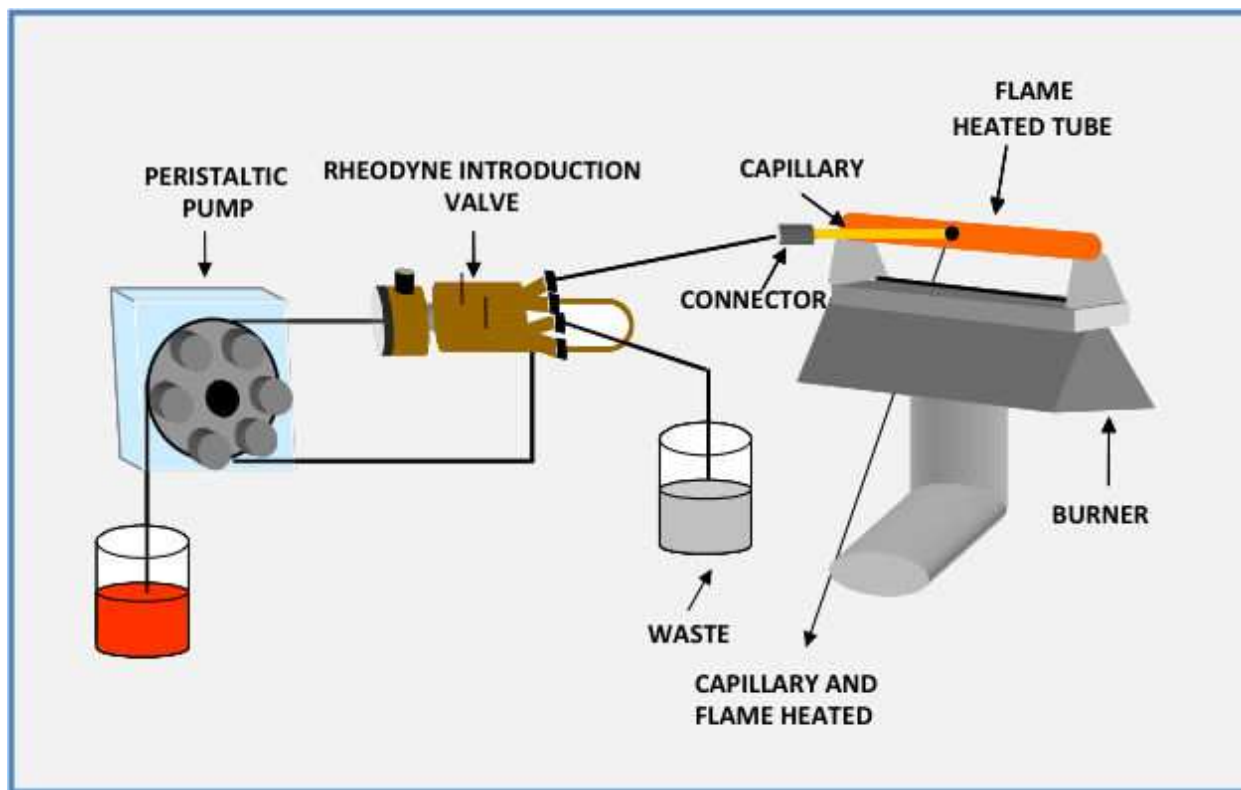


Figure 1. Schematic arrangement of the TS-FF-AAS system (adapted from Davies & Berndt 2003[59].

The sample was introduced into the system using a manual Rheodyne valve (Figure 1), after which it was transported to the ceramic capillary in the flow of air. Since the capillary was heated simultaneously with the metal or ceramic reactor tube, the liquid was partially vaporized, forming a thermospray, and atomization occurred on arrival in the tube, generating a transient signal that was captured and stored by the software. The determination employed the height of the transient signal peak.

2.4. Optimization of carrier flow rate and sample volume

The influences of the carrier flow rate (in the range 9.0-18.0 mL min⁻¹) and the sample volume (50, 100, and 200 µL) were evaluated using a standard of 200 µg Cu L⁻¹.

2.5. Construction of analytical curve

After optimization of the system, analytical curves were constructed in the concentration range 0.1-0.4 mg Cu L⁻¹ in 0.14 mol L⁻¹ HNO₃. Additions of analyte were made to the sample mixed with an equal volume of 0.14 mol L⁻¹ HNO₃. The detection limit (DL) was calculated from 12 blank readings for each type of tube (metal or ceramic).

3. Results and discussion

3.1. Optimization of carrier flow rate and sample volume

Good peak reproducibility was achieved when samples were injected into the air flow as carrier. When samples were injected into $0.14 \text{ mol L}^{-1} \text{ HNO}_3$, used as the carrier, there was a rise in the baseline (as expected, due to increase of the blank), followed by a fall due to cooling of the metal or ceramic tubes. This cooling was significant, since no transient signals were obtained following injection of standards, indicating that the temperature within the tubes was insufficient to atomize the analyte, which remained dispersed in the carrier solution. This confirmed the findings of earlier work that the use of air (or other gas) as the carrier avoids dilution and dispersion of the sample. Here, all analyses were performed using air as the carrier, not only because it was less expensive than use of a solution, and minimized waste generation, but also because it enabled the TS-FF-AAS system to be used to determine copper, which would not have been possible using a solution as the carrier.

Figure 2 shows the influence of the carrier (air) flow rate, in the range $9.0\text{--}18.0 \text{ mL min}^{-1}$, on the absorbance values obtained using $50 \mu\text{L}$ of a standard of $200 \mu\text{g Cu L}^{-1}$ in $0.14 \text{ mol L}^{-1} \text{ HNO}_3$, using both tubes. In the case of the metal tube, lower absorbance values were obtained at low flow rates, because the sample arrived slowly at the atomizer, increasing the measurement duration and resulting in an unpredictable and erratic vaporization. Hence, as the flow rate was increased, the absorbance also increased due to a more homogeneous vaporization of the sample [23,27,58].

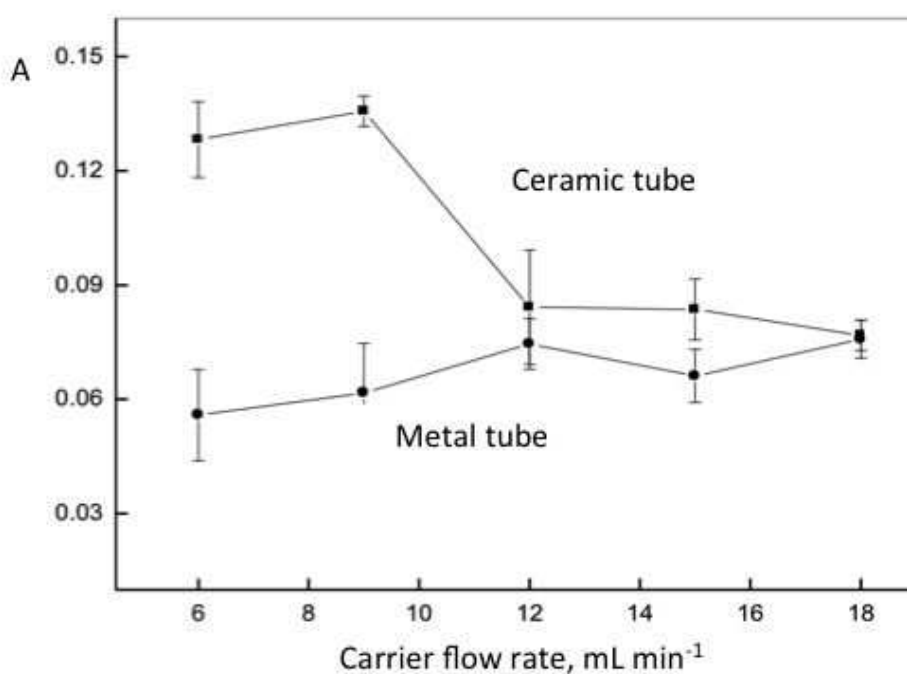


Figure 2. Influence of carrier (air) flow rate on the absorbance obtained for $50 \mu\text{L}$ of a solution of $200 \mu\text{g Cu L}^{-1}$ in $0.14 \text{ mol L}^{-1} \text{ HNO}_3$, using the metal and ceramic tubes.

This increase proceeded up to a carrier flow rate of 12.0 mL min^{-1} , above which there was no significant variation in absorbance. The highest absorbance value was obtained at a flow rate of 18.0 mL min^{-1} , which was therefore selected as the best flow rate to use with the metal tube.

When the ceramic tube was used, maximum absorbance was achieved at a carrier flow rate of 9.0 mL min^{-1} . At higher flow rates, the residence time of the liquid in the heated section of the ceramic capillary was considerably diminished, reducing the time available for evaporation of the liquid, so that the sample was not delivered in the form of vapor/aerosol, but rather as a flow of liquid. The temperature within the tube decreased, and the color of the tube changed from ruby-red to opaque grey. It was also possible to see droplets emerging from the atomizer tube. Hence, the absorbance values did not increase, while greater variability in the signal resulted in elevated standard deviation values. A flow rate of 3.0 mL min^{-1} was selected, at which the absorbance signal was maximized, and the standard deviation was minimized.

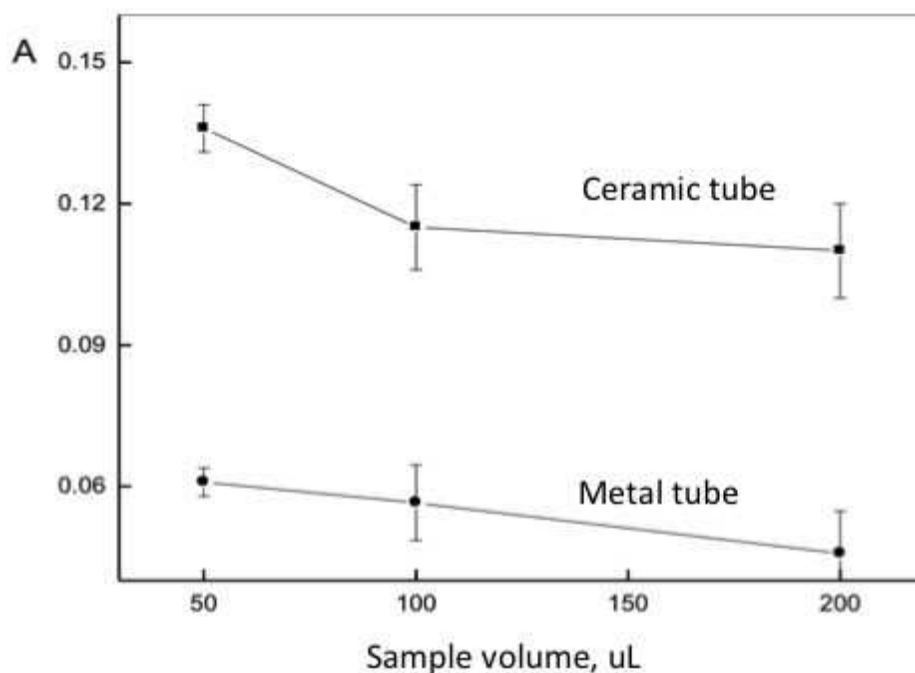


Figure 3. Influence of sample volume on the absorbances obtained for a solution of $200 \mu\text{g Cu L}^{-1}$ in $0.14 \text{ mol L}^{-1} \text{HNO}_3$, using carrier flow rates of 9.0 and 18.0 mL min^{-1} for the ceramic and metal tubes, respectively.

The sample volume was varied between 50 and $200 \mu\text{L}$, using carrier flow rates of 18.0 and 9.0 mL min^{-1} for the metal and ceramic tubes, respectively. The results (Figure 3) revealed that for both tubes a sample volume of $50 \mu\text{L}$ generated the highest absorbance value, with a low standard deviation, reflecting good repeatability in the experimental measurements. When $100 \mu\text{L}$ of sample was used, there was a slight cooling of the ceramic capillary, and consequently of the atomization tubes, while there was no increase in the absorbance values. At a sample volume of $200 \mu\text{L}$, the ceramic capillary and the tube

were substantially cooled, and there was no homogeneous thermospray formation, with erratic generation of droplets that acted to disperse the light radiation (probably to a large degree, since the deuterium lamp was unable to fully correct the resulting background signal). The unpredictable atomization resulted in very high standard deviation values. Using air as the carrier, a sample volume of 50 μL was selected for the subsequent measurements, due to greater atomization homogeneity, satisfactory absorbance for a 30 mg Cu L^{-1} standard, and a low SD value.

3.2. Construction of analytical curves

Figure 4 illustrates the results obtained for the analytical curve in the concentration range 0.1–0.4 $\mu\text{g Cu L}^{-1}$ in 0.14 $\text{mol L}^{-1}\text{HNO}_3$, using the optimized conditions of the TS-FF-AAS system. The transient signals were repeatable, and (for both tubes) the curve was linear in the concentration range studied. A two-fold greater sensitivity was achieved using the ceramic tube.

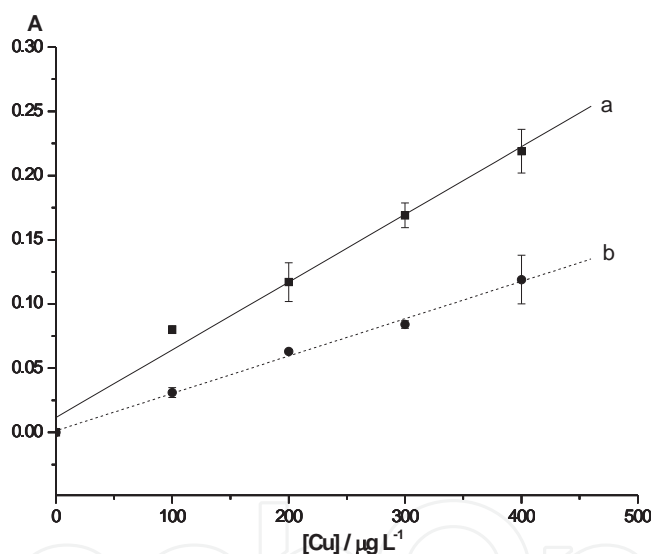


Figure 4. Regression lines fitted to the analytical curves of Cu obtained using the ceramic tube (a) and the metal tube (b) Equations of the lines: $A = 1.16 \times 10^{-2} + 5.27 \times 10^{-4}(\text{Cu})$ (ceramic tube); $A = 1.20 \times 10^{-3} + 2.91 \times 10^{-4}(\text{Cu})$ (metal tube).

Figure 5 illustrates the results obtained for the analytical curves constructed using concentrations of Cu in the range 100–400 $\mu\text{g L}^{-1}$, with additions of analyte in 0.14 $\text{mol L}^{-1}\text{HNO}_3$ to equal volumes of sample, under the optimized TS-FF-AAS system conditions. The presence of 75.8 $\mu\text{g Cu L}^{-1}$ in the sample was calculated from curve (a), obtained using the ceramic tube. This value was slightly above the detection limit (Table 1), although below the concentration of the first point of the analytical curve. In the case of the metal tube (curve (b)), a Cu concentration of 80.0 $\mu\text{g L}^{-1}$ was below the detection limit for this tube, but was nevertheless in agreement with the result obtained for the ceramic tube.

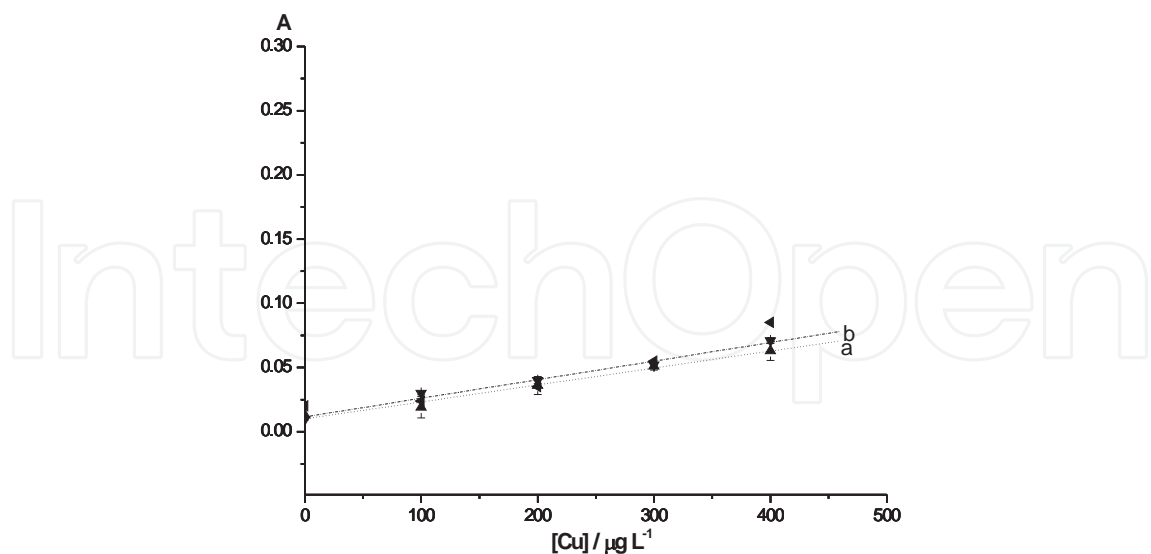


Figure 5. Regression lines fitted to the analytical curves of Cu in 1:1 mixtures of fuel samples and standards prepared in 0.14 mol L⁻¹ HNO₃, obtained using the ceramic tube (a) and the metal tube (b) Equations of the lines: A = 1.00x10⁻² + 1.32x10⁻⁴ (Cu) (ceramic tube); A = 1.16x10⁻² + 1.45x10⁻⁴ (Cu) (metal tube).

Analytical characteristics		Ceramic tube	Metal Tube
HNO ₃	Detection limit, DL (μg L ⁻¹)	55.6	56.0
	Characteristic concentration, C _o (μg L ⁻¹)	8.35	15.1
	Analytical curve interval (μg L ⁻¹)	100 – 400	
	Correlation coefficient (r)	0.9930	0.9978
	Analytical frequency (h ⁻¹)	26	100
HEAF	Detection limit, DL (μg L ⁻¹)	64.5	128
	Characteristic concentration, C _o (μg L ⁻¹)	33.3	30.3
	Analytical curve interval (μg L ⁻¹)	100 – 400	
	Correlation coefficient (r)	0.9918	0.9927
	Analytical frequency (h ⁻¹)	53	82

Table 2. Analytical characteristics for determination of Cu using the TS-FF-AAS system with ceramic and metal tubes.

The analytical parameters obtained for the determination of Cu under the optimized conditions of the TS-FF-AAS system are provided in Table 2. The analytical curves were linear for a concentration range of 100-400 μg Cu L⁻¹ in 0.14 mol L⁻¹ HNO₃. The system could be considered to be sensitive, with characteristic concentrations of 8 and 15 μg Cu L⁻¹ for the ceramic and metal tubes, respectively, and analysis frequencies (using HNO₃ medium) of 26

and 100 determinations per hour, respectively. Better analytical performance of the system was achieved using the ceramic tube, compared to the metal tube. The data showed that the TS-FF-AAS technique was more sensitive than FAAS, with nine-fold (ceramic tube) and five-fold (metal tube) increases in sensitivity, relative to FAAS with pneumatic nebulization, for which the characteristic concentration was $77 \mu\text{g L}^{-1}$. The increase in power of detection obtained using the ceramic tube was around twice that for the metal tube. The sensitivity for determination of copper using the ceramic tube was therefore two-fold that obtained using the metal tube.

4. Conclusions

The TS-FF-AAS system can be used to determine copper at low concentrations, using either metal (Inconel) or ceramic (Al_2O_3) tubes as atomizers. Following optimization considering the most important experimental variables affecting atomization, these systems provided significantly improved detection limits for Cu determination, with nine-fold (ceramic tube) and five-fold (metal tube) increases in sensitivity, compared to traditional FAAS with pneumatic nebulization. The TS-FF-AAS technique is simple, fast, effective, and inexpensive. It requires low volumes of sample (as little as $50 \mu\text{L}$) and reagents, and reduces waste generation. The method offers a useful new alternative for the determination of copper in alcohol.

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References

- [1] Lobo, FA, Gouveia, D, Rosa, AH, Oliveira, AP, Pereira-Filho, ER, Fraceto, LF, Dias-Filho, N L. Comparison of the univariate and multivariate methods in the optimization of experimental conditions for determining Pb, Cu, Ni and Cd in biodiesel by GFAAS. *Fuel*, 2009;88:1907-14.

- [2] Saint'pierre T, Aucélio R Q, Curtius A J. Trace Elemental determination in alcohol automotive fuel by electrothermal atomic absorption spectrometry. *Microchemical Journal* 2003;75: 59-97.
- [3] Oliveira, AP, Gomes Neto, JA, Moraes, M, Lima, EC. Direct determination of Al, As, Cu, Fe, Mn and Ni in fuel ethanol by simultaneous GFAAS using integrated platforms pretreated with W-Rh permanent modifier together with Pd+Mg modifier. *Atomic Spectroscopy* 2002;23:190-5.
- [4] Oliveira, AP, Gomes Neto, JA., Moraes, M, Lima, EC. Simultaneous determination of Al, As, Cu, Fe, Mn and Ni in Fuel Ethanol by GFAAS. *Atomic Spectroscopy* 2002;23: 39-43.
- [5] Oliveira, AP, Okumura, LL, Gomes Neto, JA, Moraes M. Avaliação do método das adições de analito para a determinação de sódio em álcool combustível por espectrometria de emissão atômica em chama. *Eclética Química* 2002;27:285-91.
- [6] Bettinelli, M, Spezia, S, Baroni, U, Bizzarri, G. The use of reference materials in the fossil fuels quality control. *Mikrochim. Acta* 1996;123:217-30.
- [7] Iantcheva, M. Atomic absorption spectrophotometry determination of aluminium and vanadium in navy oils and related draw materials. *Anal. Lab* 1996;5:31-5
- [8] Liang, L, Horvat, M, Danilchik, P. A novel analytical method for determination of picogram levels of total mercury in gasoline and other petroleum based products. *Sci. Total Envir.* 1996;187: 57-64
- [9] Misselwitz, R, Sengutta, U. Determination of elements in oily matrices. *Laborpraxis* 1997;21:41-8
- [10] Kowalewska Z, Bulska E, Hulanicki A. Organic palladium and palladium-magnesium chemical modifiers in direct determination of lead in fractions from distillation of crude oil by electrothermal atomic absorption analysis. *Spectrochimica. Acta, Part B* 1999;54:835-43
- [11] Zięba-Palus J, Kościelniak P. An analysis of the similarity of motor oils on the basis of their elemental composition. *Forensic Science International* 2000;112:81-90.
- [12] Meeravali NN, Kumar, SJ. The utility of a W-Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphta by transverse heated electrothermal atomic absorption spectrometer. *Journal. Analytica. Atomic. Spectrometry* 2001;16:527-32.
- [13] Sant'pierre TD, Dias, LF, Pozebon D, Aucélio RQ, Curtius AJ, Welz B. Determination of Cu, Mn, Ni and Sn in gasoline by electrothermal vaporization inductively coupled plasma mass spectrometry, and emulsion sample introduction. *Spectrochim. Acta Part B* 2002;57:1991-2001.

- [14] Giacomelli MBO, da Silva JBB, Sain't Pierre TD, Curtius A. Use of iridium plus rhodium as permanent modifier to determine As, Cd and Pb in acids and ethanol by electrothermal atomic absorption spectrometry. *Microchemical Journal* 2004;77: 151-6
- [15] Vale MGR, Damin ICF, Klassen A, Silva MM, Welz B, Silva AF, Lepri FG. Method development for the determination of nickel in petroleum using line-source and high-resolution continuum-source graphite furnace atomic absorption spectrometry. *Microchemical J.* 2004;77:131-40
- [16] Villafranca AC. Avaliação da espectrometria de absorção atômica com nebulização térmica em tubo aquecido em chama (TS-FF-AAS) para determinação de Cd, Cu, Pb e Zn em álcool combustível e óleo diesel. 2004. 144f. Tese (Doutorado em Química) – Instituto de Química, Universidade Estadual Paulista, Araraquara.
- [17] Lepri FG, Welz B, Borges DLG, Silva AF, Vale MGR, Heitmann U. Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Analytica Chimica Acta* 2006;558:195-200.
- [18] Korn MGA, do Santos, DSS, Welz, B, Vale MGR, Teixeira AP, Lima DC, Ferreira SLC. Atomic spectrometric methods for the determination of metals and metalloids in automotive fuels - A review. *Talanta* 2007;73:1-11
- [19] Amorim Filho VR, Caldas NM, Raposo Junior JL, Flumignan DL, de Oliveira JE, Gomes Neto JA. Simultaneous Determination of Ba, Cr, Mo (Group 1), and Cu, Fe, Ni, and Pb (Group 2) in Commercial Fuel Ethanol by Graphite Furnace AAS. *Atomic Spectroscopy*, 2008;29:230-35.
- [20] Alves VN, Mosquetta R, Melo Coelho NM, Bianchin JN, DiPietroRoux KC, Martendal E, Carasek E. Determination of cadmium in alcohol fuel using Moringa oleifera seeds as a biosorbent in an on-line system coupled to FAAS. *Talanta* 2010;80:1133-8.
- [21] Lobo FA, Gouveia D, Oliveira AP, Romão LP, Fraceto LF, Dias Filho NL, Rosa A H. Development of a method to determine Ni and Cd in biodiesel by graphite furnace atomic absorption spectrometry. *Fuel* 2011;90:142–6.
- [22] Silva CS, Oreste EQ, Nunes AM, Vieira MA, Ribeiro AS. Determination of mercury in ethanol biofuel by photochemical vapor generation. *J. Anal. Atomic Spectrom.* 2012;27:689-94.
- [23] Gáspar A, Berndt H. Thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) — a simple method for trace element determination with microsamples in the $\mu\text{g/l}$ concentration range. *Spectrochimica Acta Part B: Atomic Spectroscopy* 2000.;55:587-97
- [24] Gáspar A, Sézales E, Berndt H. Analysis of submicroliter samples using thermospray flame furnace atomic absorption spectroscopy. *Anal. and Bioanal. Chem.* 2002;372: : 136-40

- [25] Zeng C, Hu, Y, Luo J. Ionic liquid-based hollow fiber supported liquid membrane extraction combined with thermospray flame furnace AAS for the determination of cadmium. *MicrochimicaActa* 2012;177:53-8
- [26] Miranda K, Dionísio AGG, Pessoa Neto OD, Pereira-Filho ER. Determination of Cd levels in smoke condensate of Brazilian and Paraguayan cigarettes by Thermospray Flame Furnace Atomic Absorption Spectrometry (TS-FF-AAS). *Microchem. J.* 2012;100:27-30
- [27] Tarley CRT, Arruda MAZ. A sensitive method for cadmium determination using an on-line polyurethane foam preconcentration system and thermospray flame furnace atomic absorption Spectroscopy. *Analytical Sciences* 2004;20:961-6.
- [28] [28]Zeng C, Yang F, Zhou N. Hollow fiber supported liquid membrane extraction coupled with thermospray flame furnace atomic absorption spectrometry for the speciation of Sb(III) and Sb(V) in environmental and biological samples. *Microchem. J.* 2011;98:307-11
- [29] Rezende HC, Nascentes CC, Coelho NMM. Cloud point extraction for determination of cadmium in soft drinks by thermospray flame furnace atomic absorption spectrometry. *Microchem. J.* 2011;97:118-21
- [30] Sepulveda EG, Fuentes AA, Hinojosa JN. On-line preconcentration system coupled to thermospray flame furnace-AAS for cadmium determination at sub $\mu\text{g L}^{-1}$ levels in seawater. *Química Nova* 2011;34:700-703.
- [31] Bezerra MA, Lemos VA, Garcia JS, da Silva, DG, Araujo AS, Arruda MAZ. Thermospray generation directly into a flame furnace-An alternative to improve the detection power in atomic absorption spectrometry. *Talanta*, . 2010;82:437-443
- [32] Miranda K, Pereira-Filho ER. Potentialities of thermospray fame furnace atomic absorption spectrometry (TS-FF-AAS) in the fast sequential determination of Cd, Cu, Pb and Zn. *Analytical Methods* 2009;1: 215-219
- [33] Gomes MS, Pereira-Filho ER. Ti and Ni tubes combined in thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) for the determination of copper in biological samples. *Microchemical Journal* 2009;93:93-8
- [34] Da-Col JA, Domene SMA, Pereira-Filho ER. Fast Determination of Cd, Fe, Pb, and Zn in Food using AAS. *Food Anal Methods* 2009;2:110-115
- [35] Wu P, He S, Luo B, Hou X. Flame Furnace Atomic Absorption Spectrometry: A Review. *Applied Spectroscopy Reviews* 2009;44:411-37
- [36] Andrade FP, Nascentes CC, Costa LM, Pereira-Filho ER. Cadmium and Lead Cloud Point Preconcentration and Determination in Tobacco Samples by Thermospray Flame Furnace Atomic Absorption Spectrometry. *J. Brazilian Chem. Soc.* 2009;20:1460-6
- [37] Brancalion ML, Sabadini E, Arruda MAZ. Thermospray nebulization for flame furnace atomic absorption spectrometry - Correlations between spray formation and

- cadmium analytical sensitivity. *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009;64:89-94
- [38] Lemos VA, Bezerra MA, Amorim FAC. On-line preconcentration using a resin functionalized with 3,4-dihydroxybenzoic acid for the determination of trace elements in biological samples by thermospray flame furnace atomic absorption spectrometry. *Journal of Hazardous Materials* 2008;157:613-9
- [39] Schiavo D, Nobrega JA. Interferences in Thermospray Flame Furnace AAS: Co and Mn Behavior. *Spectroscopy Letters* 2008;41:354-60
- [40] Lobo FA, Villafranc, AC, de Oliveira AP, de Moraes M. Evaluation and Application of TS-FF-AAS System Using Ceramic Tube as Atomization Cell for Tin Determination in Canned Foods. *Atomic Spectroscopy* 2008;29:186-92
- [41] Matos GD, Arruda MAZ. Improvements in cobalt determination by thermospray flame furnace atomic absorption spectrometry using an on-line derivatization strategy. *Talanta* 2008;76:475-8
- [42] Coelho LM, Bezerra MA, Arruda MAZ, Bruns RE, Ferreira SLC. Determination of Cd, Cu, and Pb after cloud point extraction using multielemental sequential determination by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). *Separation Science and Technology* 2008;43:815-27
- [43] Wu P, Gao Y, Cheng G, Yang W, Lv Y, Hou X. Selective determination of trace amounts of silver in complicated matrices by displacement-cloud point extraction coupled with thermospray flame furnace atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry* 2008;23:752-7
- [44] Schiavo D, Neira JY, Nobrega JA. Direct determination of Cd, Cu and Pb in wines and grape juices by thermospray flame furnace atomic absorption spectrometry. *Talanta* 2008;76:1113-8
- [45] Lobo FA, Oliveira AP, Villafranca AC, Moraes M. Comparison of metallic and ceramic tubes as atomization cells for tin determination by TS-FF-AAS. *Atomic Spectroscopy* 2007;28:17-23
- [46] Rosini F, Nascentes CC, Neira JY, Nobrega JA. Evaluation of selenium behavior in thermospray flame furnace atomic absorption spectrometry. *Talanta* 2007;73:845-9
- [47] Brancalion ML, Sabadini E, Arruda MAZ. Description of the thermospray formed at low flow rate in thermospray flame furnace atomic absorption Spectrometry based on high-speed images. *Analytical Chemistry* 2007;79:6527-33
- [48] Amorim FAC, Bezerra MA. Online preconcentration system for determining ultra-trace amounts of Cd in vegetal samples using thermospray flame furnace atomic absorption spectrometry. *Microchimica Acta* 2007;159:183-9

- [49] Petrucelli GA, Poppi RJ, Mincato RL, Pereira-Filho ER. TS-FF-AAS and multivariate calibration: A proposition for sewage sludge slurry sample analyses. *Talanta* 2007;71:620-6
- [50] Wu P, Zhang Y, Lv Y, Hou X. Cloud point extraction-thermospray spectrometry for determination of flame quartz furnace atomic absorption ultratrace cadmium in water and urine. *SpectrochimicaActa Part B Atomic Spectroscopy* 2006;61:1310-4
- [51] Petrucelli GA, Stocco, PK, Bueno MIMS, Pereira-Filho ER. Tube atomizers in thermospray flame furnace atomic absorption spectrometry: characterization using X-ray fluorescence, scanning electron microscopy and chemometrics. *Journal of Analytical Atomic Spectrometry* 2006;21:1298-1304
- [52] Lobo FA, Villafranca AA, Oliveira AP, Moraes M. Sistema TS-FF-AAS com chamaacetileno-arcomoalternativaemrelação à chamaacetileno-óxidonitrosoem FAAS nadeterminação de estanho. *Eclética Química* 2005;30:61-68.
- [53] González E, Ramón A, Medina V, Neira J, Urcesino G. Espectrofotometria de Absorción Atómica con Tubo en La Llama: Aplicación en la Determinación Total de Cadmio, Plomo y Zinc en Aguas Frescas de Mar y Sedimentos Marino. *Química Nova* 2004; 27:873-7
- [54] Donati GL, Nascentes CC, Nogueira ARA, Arruda MAZ, Nobrega JS. Acid extraction and cloud point preconcentration as sample preparation strategies for cobalt determination in biological materials by thermospray flame furnace atomic absorption spectrometry. *Microchemical Journal* 2006;82:189-95
- [55] Pereira MG, Pereira-Filho ER, Berndt H, Arruda, MAZ. Determination of cadmium and lead at low levels by using preconcentration at fullerene coupled to thermospray flame furnace atomic absorption spectroscopy. *SpectrochimicaActaPart B Atomic-Spectroscopy* 2004;59:515-21
- [56] Nascentes C, Arruda MAZ, Nogueira ARA, Nobrega JA. Direct determination of Cu and Zn in fruit juices and bovine milk by thermospray flame furnace atomic absorption spectroscopy. *Talanta* 2004;64:912-7.
- [57] Davies J, Berndt H. Improvements in thermospray flame furnace atomic absorption spectroscopy. *AnalyticaChimicaActa* 2003;479:215-23
- [58] Pereira-Filho ER, Berndt H, Arruda MAZ. Simultaneous sample digestion and determination of Cd, Cu and Pb in biological samples using thermospray flame furnace atomic absorption spectroscopy (TS-FF-AAS) with slurry sample introduction. *Journal of Analytical Atomic Spectrometry* 2002;17:1308-15

