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). Electrothermal atomizers 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.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Matrix</th>
<th>Sample preparation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite furnace atomic absorption spectrometry (GFAAS)</td>
<td>Fuel oil</td>
<td>Microwave digestion</td>
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<tr>
<td>Flame atomic absorption spectrometry</td>
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<td>Atomic fluorescence spectrometry with cold vapor generation</td>
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<td>Graphite furnace atomic absorption spectrometry</td>
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<td>Graphite furnace atomic absorption spectrometry</td>
<td>Crude fuel oil</td>
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<td>Flame atomic absorption spectrometry</td>
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<td>Graphite furnace atomic absorption spectrometry</td>
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<td>Inductively coupled plasma mass spectrometry (ICP-MS)</td>
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<td>Flame atomic absorption spectrometry</td>
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<tr>
<td>Graphite furnace atomic absorption spectrometry</td>
<td>Ethyl alcohol</td>
<td>Dilution in HNO₃</td>
<td>3,4</td>
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<tr>
<td>Graphite furnace atomic absorption spectrometry</td>
<td>Ethyl alcohol</td>
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<tr>
<td>Graphite furnace atomic absorption spectrometry</td>
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<td>Graphite furnace atomic absorption spectrometry with a high-resolution continuum source (HR-CS-GFAAS)</td>
<td>Crude oil</td>
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<td>Atomic absorption spectrometry with thermal nebulization in a tube heated in a flame (TS-FF-AAS)</td>
<td>Ethyl alcohol fuel and gasoline</td>
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<tr>
<td>Graphite furnace atomic absorption spectrometry with a high-resolution continuum source</td>
<td>Crude oil</td>
<td>Oil-water emulsion</td>
<td>17</td>
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</tbody>
</table>
Table 1. Analytical methods for the determination of inorganic contaminants in fuels.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Matrix</th>
<th>Sample preparation</th>
<th>Reference</th>
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<tbody>
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<td>Atomic absorption spectrometry</td>
<td>Gasoline, diesel, ethyl alcohol and biodiesel</td>
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<tr>
<td>Flame atomic absorption spectrometry</td>
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<td>Solid phase extraction</td>
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<tr>
<td>Graphite furnace atomic absorption spectrometry</td>
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<td>Emulsion</td>
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<tr>
<td>Atomic absorption spectrometry with vapor generation (VP-FAAS)</td>
<td>Ethyl alcohol</td>
<td>Treatment with acid under UV irradiation</td>
<td>22</td>
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</table>

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 (Al₂O₃).

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 (λ = 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 Al₂O₃ (>99.8%), resistant to temperatures up to 1900 °C, with Ø_{ext} = 1.6 mm and two orifices with Ø_{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, Ø_{int} = 10.0 mm, Ø_{ext} = 12.0 mm, 6 orifices with Ø = 2.5 mm, perpendicular to an orifice with Ø = 2.0 mm), and a ceramic tube (99.9% Al₂O₃, length 100 mm, Ø_{int} = 10.0 mm, Ø_{ext} = 12.0 mm, 6 orifices with Ø = 2.5 mm, perpendicular to an orifice with Ø = 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 ± 1°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 HNO₃ (~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 HNO₃ (Synth).

The HEAF samples were prepared by mixing the fuel with an equal volume of 0.14 mol L⁻¹ HNO₃ 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)].

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 200μL) were evaluated using a standard of 200μg 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 0.14mol 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 mol L\(^{-1}\) 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 9.0-18.0 mL min\(^{-1}\), on the absorbance values obtained using 50 μL of a standard of 200 μg Cu L\(^{-1}\) in 0.14 mol L\(^{-1}\) 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](image-url)
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](image-url)  
**Figure 3.** Influence of sample volume on the absorbances obtained for a solution of 200 μg CuL\(^{-1}\) in 0.14 mol L\(^{-1}\) 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 μL, 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 μL generated the highest absorbance value, with a low standard deviation, reflecting good repeatability in the experimental measurements. When 100 μL 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 μL, 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 μg Cu L⁻¹ in 0.14 mol L⁻¹ HNO₃ 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](image)

**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 μg L⁻¹, with additions of analytein 0.14 mol L⁻¹ HNO₃ to equal volumes of sample, under the optimized TS-FF-AAS system conditions. The presence of 75.8 μg 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 μg L⁻¹ was below the detection limit for this tube, but was nevertheless in agreement with the result obtained for the ceramic tube.
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 μg 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 (Al₂O₃) 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 μL) and reagents, and reduces waste generation. The method offers a useful new alternative for the determination of copper in alcohol.

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