Determination of copper, iron, nickel and zinc in ethanol fuel by energy dispersive X-ray fluorescence after pre-concentration on chromatography paper

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A B S T R A C T
This paper presents an alternative analytical method employing energy dispersive X-ray fluorescence (EDXRF) to determine copper, iron, nickel and zinc ions in ethanol fuel samples after a pre-concentration procedure. Our pre-concentration strategy utilizes analyte retention on cation exchange chromatography paper, a convenient substrate for direct EDXRF measurements. The repeatability, expressed in terms of RSD of standard solutions containing 0.25 μg mL−1 of Cu, Fe, Ni and Zn, and calculated from fifteen consecutive measurements, was 2.5, 2.8, 3.0, and 2.7%, respectively. The limits of detection (LOD), defined as the analyte concentration that gives a response equivalent to three times the standard deviation of the blank (n = 10), were found to be 13, 15, 15 and 12 μg L−1 for Cu, Fe, Ni and Zn, respectively. The proposed method was applied to Cu, Fe, Ni and Zn determination in hydrated ethanol fuel samples collected from different gas stations.

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1. Introduction

Ethyl alcohol, obtained from a renewable source, has gained increasing interest as a fuel substitute for conventional hydrocarbon fuels with the possibility of improving urban air quality, decreasing the emission of greenhouse gases, and minimizing dependence on oil [1]. As a result, ethanol has been used as fuel in a hydrated form or an additive in gasoline [2].

However, to use ethanol as fuel, one must be able to guarantee its quality and test for contaminants. Ethanol fuel contains inorganic contaminants, such as metal ions, which are introduced during production, transport and storage [3]. The presence of these species, even at low concentrations, can negatively affect engine performance, intensify the corrosive properties of ethanol and increase the emission levels of pollutants [4]. Therefore, the development of analytical methods for the determination of metallic contaminants in ethyl alcohol fuel to ensure quality is a relevant area of research. The current specification for ethanol fuel imposed by ANP, the Brazilian Agency for Oil, Natural Gas and Biofuel [5], establishes a maximum level of iron in hydrated fuel ethanol not higher than 5 mg kg−1, while the copper level must be lower than 0.07 mg kg−1. American standard specification [6], in consonance with the European [7], defines a limit of 0.1 mg kg−1 as the maximum allowed concentration for copper. There are still no rules in legislations for other metallic species such as nickel and zinc.

The determination of metals in ethanol-based matrices using spectrometric techniques has been reported in the literature. Inductively coupled plasma optical emission spectrometry (ICP-OES) is a sensitive technique, but high alcohol content may preclude plasma stability [8]. Flame atomic absorption spectrometry (F AAS) has been used for the determination of metals in ethanol fuel, however the direct introduction of fuel samples may cause flames to become excessively fuel-rich and unstable [9]. Chromogenic reagents have also been used for metal determination in ethanol fuel samples by spectrophotometry, but these methods frequently require time-intensive pretreatment measures, including heating and concentrated acids [10].

Energy dispersive X-ray fluorescence (EDXRF) is an attractive multielement and nondestructive technique that is environmentally friendly because it minimizes the number of sample preparation steps and, therefore, the waste generated [11,12]. Analytical methods involving EDXRF do not typically require the sample to be subjected to any drastic or time-consuming treatment, such as concentrated acids, delayed heating or dilution in organic solvents [1]. Additionally, there is the possibility of multielement analysis by direct measurements on solid support after the preconcentration procedure. This procedure avoids an additional elution step after the preconcentration procedure necessary to recover the species, thereby minimizing sample handling [13]. This approach was previously used for water [14], environmental samples [15],

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engine oil [16], gasoline [1] and ethanol fuel analysis [17]. For this purpose, different solid supports have been used such as cellulose filter [14,17], C-18 or chelating solid phase [16,18], silica gel [19] and ion exchange resins [20,21].

The binding functional groups of the ion exchange cellulose chromatography paper, which are chemically immobilized on the cellulose backbone, provide good chemical stability and uniformity of coverage on all surfaces of the membrane [22]. This material has excellent ion exchange properties combined with a desired hydrophilic nature and has been used for separation of trace metals [23], including determinations by EDXRF after preconcentration step [24,25]. However, the use of ion exchange paper in the combination of EDXRF analysis and preconcentration techniques, to the best of our knowledge, has not yet been described for ethanol fuel analysis.

In this work, a practical procedure for the determination of metal ions (copper, iron, nickel and zinc) in ethanol fuel samples by EDXRF after a preconcentration step is proposed. Determination of iron, copper, nickel and zinc in ethanol fuel samples by EDXRF without pre-concentration was not possible because the technique is not sensitive enough to quantify trace elements. Therefore, pre-treating the sample using ion exchange cellulose chromatography paper, as proposed in this work, is a convenient step that makes this analysis possible. A suitable pre-concentration procedure was obtained when analyses retention on chromatography paper was performed by filtration and the paper functioned as a substrate for direct EDXRF measurements after sample drying.

2. Experimental

2.1. Apparatus

A dispersive X-ray fluorescence spectrometer equipped with a rhodium tube and Si(Li) semiconductor detector was used for the analysis (Shimadzu EDX 800, Kyoto, Japan). For the analysis, we used an irradiation time of 100 s, a tube voltage of 40 kV, a tube current of 30 mA and an air atmosphere. The analytical lines were iron, 6.400 keV (Kα); copper, 8.042 keV (Kα); nickel, 7.473 keV (Kα); and zinc, 8.632 keV (Kα). All measurements were based on the integrated peak intensity.

A Varian (Mulgrave, Australia) Vista simultaneous inductively coupled plasma optical emission spectrometry instrument with axial viewing, equipped with charge coupled device (CCD), Sturman–Master chamber and a V-Groove nebulizer, was used as a comparative method. The metal determinations were carried out under manufacturer-recommended conditions for power (1.3 kW), plasma gas flow (15.0 L min⁻¹), nebulizer gas flow (0.7 L min⁻¹) and auxiliary gas flow (1.5 L min⁻¹). The analytical wavelengths selected were 324.754, 248.327, 232.003 and 213.857 nm for Cu, Fe, Ni and Zn, respectively.

A Gilson Minipuls 2 (Villiers-le-Bel, France) peristaltic pump equipped with Viton tube was employed to propel ethanol fuel samples or standard solutions onto the filter holder for the pre-concentration procedure. All pH measurements were made with a Digimed DM 20 model (São Paulo, Brazil) digital pH meter.

2.2. Reagents and samples

All solutions were prepared using analytical-grade reagents (Merck, Darmstadt, Germany) and high-purity demineralized water obtained using a Milli-Q Water System (Millipore, France). Methanol (min. 99.8%) was used to prepare the metal-based solutions. Multi-element solution (1000 µg mL⁻¹) was prepared by accurately weighing copper, iron, zinc and nickel nitrates followed by dilution with methanol. This solution was used to prepare the calibration curve in a hydrated ethanol medium (min. 95.1%). A 0.25 µg mL⁻¹ metal ions solution in a hydrated ethanol medium was used in the optimization procedure. pH adjustments were performed with HCl and NaOH (0.01 mol L⁻¹) solutions.

Multi-element aqueous standard with a content of 1000 mg L⁻¹ Cu, Fe, Zn and Ni was supplied by Merck (Darmstadt, Germany) and employed to assure the concentrations of the nitrates solution by ICP OES.

Whatman Grade P81 ion exchange cellulose chromatography paper (Maidstone, England) was cut into small disks (13 mm diameter) and adapted in polycarbonate syringe filter holders (Sartorious, Germany) for the pre-concentration procedure.

Commercial hydrated ethanol fuel samples were collected at random from different gas stations in the city of Salvador, Brazil.

2.3. General procedure

First, pH samples were checked and, if necessary, adjusted to a pH of 5.0–7.5 using a minimal volume of HCl or NaOH solution (0.01 mol L⁻¹). Then a chromatography paper disk was placed into the filter holder, and 10 mL of each sample or standard solution was passed through the papers with the use of a peristaltic pump at 2.0 mL min⁻¹. The paper was taken out of the holders and dried at room temperature. The blank was prepared using the same procedure with pure hydrated ethanol. The paper disks were adapted into the center of the spectrometer cell, a polyethylene device of about 20 mm of height and 30 mm of internal diameter, using Mylar film as sample support so that it will fit properly into the XRF sample holder for the fluorescence measurements. Copper, iron, nickel and zinc were determined directly on the chromatography paper by XRF spectrometry, and the concentration of each element was calculated according to the calibration curves.

3. Results and discussion

To optimize the sorption conditions for the retention of iron, copper, nickel and zinc ions on chromatography paper, some experimental variables affecting the extraction efficiency, such as pH, sample flow rate and sample volume, were investigated. A 0.25 µg mL⁻¹ metal ions solution was used for all measurements. An X-ray fluorescence spectrum of a sample indicating the peaks used for measured each element is presented in Fig. 1.

3.1. Effect of acidity

The effect of acidity on the extraction efficiency of Fe, Cu, Ni and Zn ions from ethanol to the cation exchange chromatography paper was studied under pH values ranging from 2 to 8. With respect to this study, the pH values of sample solutions were adjusted using a minimal volume of 0.01 mol L⁻¹ HCl or NaOH. Buffer solutions were
not used to avoid adding foreign anions that could affect cation retention on the paper. Over a pH range between 2 and 4, the retention efficiency was low for all cations tested. The highest extraction efficiency was achieved between pH 4.0 and 7.5 for iron and 5.0 and 7.5 for copper, nickel and zinc. The experimental results are shown in Fig. 2. Therefore, pH values between 5.0 and 7.5 were selected as a working pH range. The pH of the samples were measured immediately before analysis and adjusted with HCl or NaOH solutions as necessary.

3.2. Effect of flow rate

The loading sample flow rate through the chromatography paper is important to consider because it affects analyte retention with respect to the solid phase and the frequency of analysis. The influence of the sample flow rate on Fe, Cu, Ni, and Zn retention on chromatography paper was investigated by varying the flow rate of the sample solution from 1.2 to 5.0 mL min\(^{-1}\). This test was performed while maintaining the sample volume at 10 mL. It was found that the retention of all four analytes was affected significantly by the flow rate. The experimental results are shown in Fig. 3. It can be seen that a flow rate of 1 mL min\(^{-1}\) provides higher intensities, meaning a better retention, i.e. higher sensitivities were obtained when lower flow rates were employed. As the flow rate can affect both the retention efficiency and sampling rate, a flow-rate value of 2.0 mL min\(^{-1}\) was chosen as a compromise between sample throughput and sensitivity.

3.3. Sample volume

One of the main advantages of direct measurements on the solid support after solid phase extraction is the potential improvement of sensitivity by increasing the sample solution volume used for analysis [26]. This can be exploited to adjust the sensitivity of the procedure as a function of the analyte concentration in the sample. This effect can be assessed by measuring the signal intensity on the chromatography paper with different volumes of solution containing the same concentration of the analytes passed through the solid phase.

The influence of sample volume was evaluated by varying the volume of the standard solution containing 0.25 \(\mu\)g mL\(^{-1}\) of each analyte between 1.00 and 25.0 mL according to the recommended procedure described in Section 2.3. As a result, linear relations were observed between the intensity signals and the sample volume, as described by the following equations:

\[
I = 4.4 \times 10^{-3} \ V + 0.018 \quad (r = 0.992), \text{ for iron}\]

\[
I = 5.5 \times 10^{-3} \ V + 0.011 \quad (r = 0.995), \text{ for copper}\]

\[
I = 8.7 \times 10^{-3} \ V + 0.007 \quad (r = 0.996), \text{ for nickel}\]

\[
I = 8.3 \times 10^{-3} \ V + 0.003 \quad (r = 0.995), \text{ for zinc}\]

where \(I\) is the intensity signal (cps) and \(V\) is the sample volume (mL).

Because a 10.0 mL sample volume was sufficient to obtain an appropriate sensitivity to determine all analytes concentration in ethanol fuel and because an excessive increase in the sample volume could impair sample throughput, this volume (10.0 mL) was chosen for the general procedure.

![Fig. 2. The effect of pH between 2 and 8 upon the retention of iron (A), nickel (B), copper (C), and zinc (D) on cation exchange chromatography paper.](image)

![Fig. 3. Effect of the flow rate on the analytical signal for iron, copper, nickel and zinc determination by EDXRF after retention of the analytes on cation exchange chromatography paper.](image)
Table 1
Analytical characteristics of the proposed method for determination of copper, iron, nickel and zinc in ethanol fuel samples by EDXRF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analyte</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical curve</td>
<td></td>
<td>$l=0.258C+0.023$</td>
<td>$l=0.225C+0.024$</td>
<td>$l=0.256C+0.024$</td>
<td>$l=0.351C+0.026$</td>
</tr>
<tr>
<td>Correlation</td>
<td></td>
<td>0.9987</td>
<td>0.9987</td>
<td>0.9982</td>
<td>0.9988</td>
</tr>
<tr>
<td>Detection limit</td>
<td>(µg L$^{-1}$)</td>
<td>13</td>
<td>15</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Quantification</td>
<td>(µg L$^{-1}$)</td>
<td>43</td>
<td>50</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>RSD, n (n=10)</td>
<td></td>
<td>2.5</td>
<td>2.8</td>
<td>3.0</td>
<td>2.7</td>
</tr>
</tbody>
</table>

* 1. intensity signal (cps µA$^{-1}$); C, concentration (µg mL$^{-1}$); 10 mL sample volume.

Table 2
Determination of copper, iron, nickel and zinc (µg L$^{-1}$) in five commercialized ethanol fuel samples through spike recovery tests with the addition of 100 µg L$^{-1}$ of each metal by the proposed method and the comparative method.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample with copper addition</td>
<td>279 ± 8</td>
<td>477 ± 8</td>
<td>255 ± 7</td>
<td>266 ± 13</td>
<td>309 ± 9</td>
</tr>
<tr>
<td>Sample without copper addition</td>
<td>181 ± 5</td>
<td>380 ± 8</td>
<td>163 ± 5</td>
<td>172 ± 16</td>
<td>211 ± 9</td>
</tr>
<tr>
<td>Copper recovery (%)</td>
<td>98</td>
<td>97</td>
<td>92</td>
<td>94</td>
<td>98</td>
</tr>
<tr>
<td>Comparative method</td>
<td>180 ± 2</td>
<td>400 ± 10</td>
<td>164 ± 3</td>
<td>171 ± 2</td>
<td>222 ± 6</td>
</tr>
<tr>
<td>Sample with iron addition</td>
<td>132 ± 4</td>
<td>214 ± 9</td>
<td>216 ± 9</td>
<td>188 ± 6</td>
<td>187 ± 8</td>
</tr>
<tr>
<td>Sample without iron addition</td>
<td>(37 ± 1)</td>
<td>122 ± 10</td>
<td>120 ± 14</td>
<td>92 ± 4</td>
<td>90 ± 7</td>
</tr>
<tr>
<td>Iron recovery (%)</td>
<td>95</td>
<td>92</td>
<td>96</td>
<td>96</td>
<td>97</td>
</tr>
<tr>
<td>Comparative method</td>
<td>39 ± 1</td>
<td>140 ± 9</td>
<td>132 ± 12</td>
<td>120 ± 1</td>
<td>92 ± 2</td>
</tr>
<tr>
<td>Sample with nickel addition</td>
<td>129 ± 7</td>
<td>256 ± 7</td>
<td>188 ± 10</td>
<td>169 ± 5</td>
<td>167 ± 7</td>
</tr>
<tr>
<td>Sample without nickel addition</td>
<td>(36 ± 6)</td>
<td>161 ± 3</td>
<td>92 ± 10</td>
<td>71 ± 2</td>
<td>71 ± 6</td>
</tr>
<tr>
<td>Nickel recovery (%)</td>
<td>93</td>
<td>95</td>
<td>96</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>Comparative method</td>
<td>37 ± 5</td>
<td>160 ± 6</td>
<td>93 ± 9</td>
<td>81 ± 9</td>
<td>72 ± 6</td>
</tr>
<tr>
<td>Sample with zinc addition</td>
<td>218 ± 9</td>
<td>248 ± 8</td>
<td>156 ± 7</td>
<td>187 ± 9</td>
<td>249 ± 17</td>
</tr>
<tr>
<td>Sample without zinc addition</td>
<td>123 ± 13</td>
<td>154 ± 15</td>
<td>58 ± 5</td>
<td>92 ± 8</td>
<td>150 ± 16</td>
</tr>
<tr>
<td>Zinc recovery (%)</td>
<td>95</td>
<td>94</td>
<td>98</td>
<td>95</td>
<td>99</td>
</tr>
<tr>
<td>Comparative method</td>
<td>140 ± 3</td>
<td>157 ± 4</td>
<td>61 ± 3</td>
<td>91 ± 3</td>
<td>180 ± 5</td>
</tr>
</tbody>
</table>

* Uncertainties are estimates of relative standard deviation based on three determinations. Values below quantification limit are given in parenthesis.

3.4. Interferences

Anions as chloride, nitrate and sulfate, and metallic species such as sodium, potassium, magnesium and calcium as well as other inorganic species can be found in ethanol fuel samples at different concentration levels. Detailed descriptions in relation to elements present in ethanol fuel and their concentrations can be found in a previously reviewed about quality control of ethanol fuel [27].

Despite EDXRF is an instrumental technique with sufficient spectral resolution for simultaneous determination of metals, the influence of select coexisting ions with respect to the retention of copper, iron, nickel and zinc on exchange cellulose chromatography paper was investigated. With this in mind, 100 µg L$^{-1}$ of some potential ions that might exist in ethanol fuel samples were added to solutions containing 0.25 µg L$^{-1}$ of Fe, Cu, Ni and Zn and then monitored according to general procedure. The effect of each species was considered as interference when the signals in the presence of the species was >5% of that obtained in the absence of the foreign ion. Under the conditions studied, species such as Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Br$^–$, CO$_3^{2–}$, CH$_3$COO$^–$, SO$_4^{2–}$, Cl$^–$, PO$_4^{2–}$, NO$_3$ $^–$ and I$^–$ did not interfere.

3.5. Analytical features and application

Using the general procedure, a series of experiments was conducted to obtain the calibration graph, precision and detection limit for the determination of each analyte. The analytical curves consisted of seven points, including the blank, and good correlation coefficients were found. Linear relations were observed between the intensity signals and the metal ion content when the analyte concentration ranged from 0.050 to 1.50 µg mL$^{-1}$. The repeatability of the proposed method was assessed by performing fifteen consecutive measurements at a concentration level of 0.25 µg mL$^{-1}$ of each metal, and expressing the result in terms of the relative standard deviation (RSD). The limits of detection (LOD) were defined as the analyte concentration that gives a response equivalent to three times the standard deviation of the blank (n = 10). Table 1 shows the analytical characteristics of the proposed method for the determination of Fe, Cu, Ni and Zn.

The proposed method was applied to the determination of iron, copper, nickel and zinc in ethanol fuel samples from different fuel distributors. To test the performance of the method, the proposed procedure was verified through spike recovery tests by adding 100 µg L$^{-1}$ of each metal to five different samples. The results were obtained as the average of three replicates of each sample and are shown in Table 2. As can be seen, the method has good accuracy and the recoveries were between 92 and 99%.

The results obtained by the proposed method were compared to the results obtained by the comparative method using ICP OES after sample digestion [8]. The results, obtained as the average of three replicates of each sample, show good agreement (Table 2). The paired t-test (95% confidence level) did not show significant differences.

4. Conclusion

The proposed procedure provides a sensitive and simple approach for the determination of iron, copper, nickel and zinc ions in hydrated ethanol fuel samples by EDXRF after application of a preconcentration step involving the retention of analytes on cation exchange chromatography paper. The method is simple and does not require the sample to be subjected to any drastic or time-consuming pretreatment. This procedure is useful for monitoring metal ions in a large number of ethanol fuel samples and can be considered to be an alternative technique for the determination of metals in ethanol fuel.

* 1. intensity signal (cps µA$^{-1}$); C, concentration (µg mL$^{-1}$); 10 mL sample volume.
Acknowledgments

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