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Article

Simple Spectrophotometric Determination of Iron in Diesel Oil after Sample Preparation Employing Extraction Induced by Emulsion Breaking

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This work reports the development of a simple and fast method for the spectrophotometric determination of Fe in diesel oil using the classic reaction with 1,10-phenanthroline after its extraction induced by emulsion breaking (EIEB). The extraction parameters of EIEB were optimized (concentration of HNO_3 and Triton X-100® in the emulsifying solution) as well as the adjustment of the pH of the final solution, a necessary step to complete the colorimetric reaction. The developed method presented a limit of detection of 0.004 mg L^{-1} and a limit of quantification of 0.013 mg L^{-1} and was applied in the analysis of six samples of diesel oil with different specifications. The results were statistically similar to those obtained by graphite furnace atomic absorption spectrometry (GF AAS). A recovery test was also performed by spiking the samples with 1.0 mg L^{-1} of Fe in the form of an organometallic compound, yielding recovery percentages between 83 and 108%.

Keywords: diesel oil, spectrophotometry, iron, extraction induced by emulsion breaking

Introduction

In Brazil, diesel oil is widely used to push a huge fleet of trucks and buses, which is responsible for the transportation of people and products throughout the country. As a consequence, the Brazilian oil company, Petrobras, has devoted a lot of effort to improving the quality of diesel oil produced in refineries due to technical, economical, and environmental issues.[1]

Diesel oil is mainly composed of hydrocarbons with 10 to 20 carbon atoms and is distilled between 170 and 370 °C, resulting in a product that is heavier than automotive gasoline.[2] It also contains small quantities of other substances, such as organic compounds, with sulfur, nitrogen, and oxygen in their structures. The oxidation of these compounds results in the formation of solid deposits, usually named gum, which is responsible for a number of problems, such as poor fuel performance and a reduction in the durability and efficiency of engines.[3-5] It is well established that the presence of metal in liquid fuels, even at trace concentrations, can enhance the appearance of gum because it catalyzes the oxidation of certain organic molecules.[6,7] According to Teixeira *et al.*,[7] Fe and Cu strongly induce the formation of gum in automotive gasoline in comparison with the weak effect of Ni, Zn, and Pb. Therefore, careful control of the concentrations of these metals in liquid fuels seems to be important to increasing the quality of these products over longer time periods.

The determination of metals in liquid fuels has been preferentially carried out using atomic spectrometry techniques, such as inductively coupled plasma mass spectrometry (ICP-MS),[8-10] inductively coupled plasma optical emission spectrometry (ICP OES),[10-13] and graphite furnace atomic absorption spectrometry (GF AAS),[14-16] due to their intrinsic sensitivity, robustness, and high productivity, especially observed in the case of plasma-based techniques. On the other hand, this instrumentation presents a high cost of acquisition, operation, and maintenance, making this kind of analysis expensive. It is important to mention that the application of these techniques is, in general, accompanied by a previous step of sample treatment, which can involve the total mineralization of samples or even their direct introduction in the form of an emulsion or microemulsion.

In 2010, our research group proposed the use of a simple extraction approach to induce the transference of metallic species from diesel oil to an aqueous phase.[17] This approach involved the formation of an emulsion between the oil sample and an aqueous acid solution containing an emulsifying agent followed by its breakdown by heating (or centrifugation), and it was called extraction induced by

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emulsion breaking (EIEB). The disruption of the emulsified system yielded two distinct phases: (*i*) an upper organic phase, composed of the restituted diesel oil, and (*ii*) a lower aqueous phase. During the process, metals were transferred to the aqueous phase, which made their quantification by GF AAS easy. Since then, EIEB has been employed in the analysis of different types of oils by our research group[18-23] and other groups around the world,[24-30] but almost always with the use of an atomic spectrometry technique for the quantification of the analytes in the obtained extracts.

This work proposes, for the first time, the use of low-cost molecular absorption spectrophotometry (in the visible region) as an analytical technique for the analysis of the extracts obtained by EIEB. The determination of Fe in the extracts was optimized in order to allow for quantification in diesel oil, which is one of the most important tasks for its quality control. We explored the classic reaction of Fe^{II} with 1,10-phenanthroline at a pH of around 4, which provided sufficient sensitivity for the quantification of Fe in the samples.

Experimental

Apparatus

The spectrophotometric determination of Fe in the extracts was carried out with a Varian Cary 60 spectrophotometer (Mulgrave, Australia) using a 10 mm quartz cuvette. The absorbance was measured at 510 nm, which represents the wavelength at which the maximum absorption of the complex Fe^{II}/1,10-phenanthroline was observed.[31]

The emulsion breakdown was induced with a temperature-controlled water bath (± 0.1 °C) maintained at 90 °C. The water bath (model NT 247) was furnished by Nova Técnica (São Paulo, Brazil). A centrifuge from Eppendorf (Hamburg, Germany), model 5804, was used to improve the separation of the phases.

The pH measurements were performed with a Digimed (São Paulo, Brazil) DM-22 pHmeter equipped with a standard combined glass electrode, also supplied by Digimed.

The determination of Fe in the samples of diesel oil by GF AAS was carried out using a method developed in our research group for the analysis of jet fuel.[32] The method was based on the introduction of the samples in the form of emulsions, but with the use of diesel oil instead of jet fuel for the preparation of the emulsions. In this case, a Varian AA240Z graphite furnace atomic absorption spectrometer (Mulgrave, Australia) equipped with a GTA 120 atomization unit and a Zeeman-effect background corrector was employed for the measurements. The atomization of Fe was done on a L'Vov platform coated with pyrolytical graphite, and the emulsions (20 µL) were introduced into the graphite tube using a PSD 120 autosampler (Varian, Mulgrave, Australia). A hollow cathode lamp of Fe was used as a radiation source, and the absorbance was measured at 248.3 nm using a spectral bandwidth of 0.2 nm. Argon gas with 99.99% purity (Linde Gases, Macaé, Brazil) was used as a protective gas.

Reagents and solutions

The deionized water employed in the preparation of aqueous solutions was obtained with a Direct-Q 3 System from Millipore (Milford, MA, USA). The deionized water always presented a resistivity of 18.2 MΩ cm or higher.

Ultrapure HNO_3 was obtained by double distillation of concentrated HNO_3 from Tedia (Fairfield, OH, USA) in a Berghof (Eningen, Germany) BSB-939-IR sub-boiling distillation system. The final concentration of the obtained concentrated acid was determined by titration with a standardized solution of NaOH.

The aqueous stock solution of Fe^{III} with a concentration of 1,000 µg mL^{-1} was supplied by SPEX (Metuchen, NJ, USA). The aqueous standard solutions used in the experiments were prepared by dilution of the stock solution with deionized water. The oil-based stock solution of Fe (organometallic form) with a concentration of 1,000 µg g^{-1} was supplied by Conostan (Houston, TX, USA). When necessary, this solution was diluted with HPLC-grade hexane (Tedia, São Paulo, Brazil) to allow the incorporation of the desired concentration of Fe into the oil samples.

The solution employed for the emulsification of the samples was prepared by careful mixing of 1.5 g of Triton X-100® (Sigma Aldrich, St. Louis, MO, USA) and 10 mL of doubly-distilled concentrated HNO_3 in 30 mL of deionized water. Then, the mixture was transferred to a 50 mL volumetric flask, and the volume was completed to the mark with deionized water.

Ascorbic acid, 1,10-phenanthroline, sodium acetate and concentrated acetic acid used in the spectrophotometric determination of Fe in the extracts were supplied by Vetec (Rio de Janeiro, Brazil).

Diesel oil samples

Six samples of diesel oil, purchased at gas stations in the city of Niterói, Rio de Janeiro, Brazil, were analyzed. They were stored in dark glass bottles until analysis. Diesel oil samples with different specifications (S10 and S500, containing a maximum sulfur concentration of 10 and 500 mg kg^{-1}, respectively) were analyzed in this

work. Sample D_1 was fortified with 1.0 mg L^{-1} of Fe (in organometallic form) and used in the optimization of the extraction conditions.

General procedure

The determination of Fe in diesel oil was performed by spectrophotometry using 1,10-phenanthroline as a chromogenic reagent after its extraction from the samples using EIEB. In the first step, 10 mL of diesel oil was mixed with 2 mL of the emulsifying solution in a 50 mL polypropylene tube. The tube was capped, and after manual vigorous agitation for approximately 60 s the formation of a homogeneous emulsion was observed. The tube containing the emulsion was immediately immersed in a water bath at 85 °C until the breakdown of the emulsion was verified, which took approximately 30 min. At this stage, two phases had already formed: (*i*) an upper phase containing the remaining diesel oil and (*ii*) a lower phase, which was formed by the aqueous acid solution containing the extracted Fe. After the heating step, the tube was centrifuged for 10 min at 5000 rpm to improve the separation of the phases, which allowed the recovery of 2 mL of aqueous extract. Afterward, the upper phase was removed with the aid of a pipette, and the lower phase (aqueous extract) was filtered through a 0.22 μm polyvinylidene fluoride (PVDF) membrane filter to remove any residual turbidity. Then, 0.50 mL of the filtered aqueous phase was transferred to a 10 mL volumetric flask, where the colorimetric reaction was carried out. For this, 1.0 mL of a 1% (m/v) ascorbic acid solution, 1.0 mL of a 0.25% (m/v) 1,10-phenanthroline solution, and 4.0 mL of an acetate buffer solution (0.50 mol L^{-1}) with a pH of 4.5 were added to the flask. The final volume was completed to 10 mL with deionized water. The color developed immediately, and the absorbance at 510 nm was measured with a 10 mm quartz cuvette. The methodological calibration was performed with aqueous solutions of Fe^{III} (0.050 to 2.0 mg L^{-1}) prepared under the same conditions employed for color development of the extracts. The experiments were always run in triplicate.

Results and Discussion

Initial evaluation of the spectrophotometric determination of Fe with 1,10-phenanthroline

Although the reaction between Fe^{II} and 1,10-phenanthroline is well-known[31] and largely used for the spectrophotometric determination of Fe in different kinds of samples, some adjustments were needed for its use in the quantification of Fe in the acid extracts from EIEB. The following factors were evaluated: (*i*) the influence of the concentration of ascorbic acid, which was used as a reducing agent to ensure that the presence of all Fe in the solution was as the Fe^{II} ion; (*ii*) the influence of the concentration of 1,10-phenanthroline, which acts as a chromogenic reagent; (*iii*) the influence of pH (and buffer solution concentration) since the extension of the reaction between Fe^{II} and 1,10-phenanthroline depends on the adjustment of the pH of the medium; and (*iv*) the influence of the order of the addition of reagents. All experiments were carried out with an aqueous solutions of Fe^{III} with a concentration of 1.0 mg L^{-1}.

The highest sensitivity was achieved when using the following conditions: (*i*) 0.10% (m/v) ascorbic acid; (*ii*) 0.025% (m/v) 1,10-phenanthroline; and (*iii*) 0.050 mol L^{-1} of acetate buffer with a pH of 4.5. The order of the addition of reagents did not influence the colorimetric reaction; therefore, the following order of addition was used: sample (standard solution); ascorbic acid solution; 1,10-phenanthroline; buffer solution. These conditions were employed in the analysis of all extracts obtained in the optimization of extraction conditions, otherwise mentioned in the specific experiment.

Influence of buffer concentration added to the final solution

After initial evaluation of the experimental conditions for the spectrophotometric determination of Fe with 1,10-phenanthroline, the influence of the concentration of acetate buffer (pH = 4.5) utilized to adjust the pH of the solution to be measured after extraction was detailed. In the experiments performed to optimize the colorimetric reaction, maximum sensitivity was observed when a 0.050 mol L^{-1} acetate buffer (pH = 4.5) final concentration was employed. However, this factor had to be studied again because the Fe extraction was performed in acidic medium, which could reduce the pH of the final solution to be measured, impairing the formation of the Fe^{II}/1,10-phenanthroline complex.

In this study, some initial extraction experiments were carried out, always using 10 mL of sample and 2 mL of an emulsifying solution containing 2.8 mol L^{-1} of HNO_3 and 2.5% (m/v) Triton X-100®. At the end of the process, 2 mL of the extract was separated in the EIEB process, but only 0.50 mL was collected, filtered, and transferred to a 10 mL volumetric flask for color development. Then, ascorbic acid and 1,10-phenanthroline were added in the concentrations previously optimized as well as variable concentrations (0.025 to 0.25 mol L^{-1}) of acetate buffer solution with a pH of 4.5. The absorbance and the final pH of the solutions were measured, and the results are displayed in Figure 1.

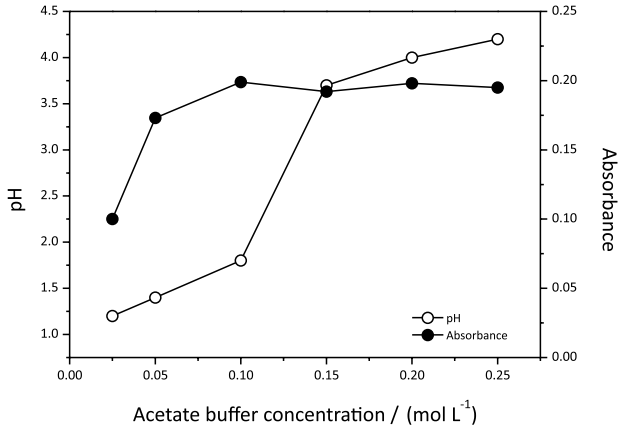

Figure 1. Influence of acetate buffer concentration on the (●) absorbance signal and (○) pH of the final solution used for the spectrophotometric determination of Fe.

As can be seen in Figure 1, the maximum absorbance was observed when the buffer concentration was between 0.10 and 0.25 mol L^{-1}. Because of the high acidity of the extracts, the use of a buffer concentration below 0.10 mol L^{-1} was not sufficient to increase the pH to a value suitable to promote the colorimetric reaction, making the absorbance lower. As expected, the pH of the final solution increased with the increase in the buffer concentration, achieving relative stability in the range of 0.15-0.25 mol L^{-1}. The pH of these solutions varied from 3.7 to 4.1, which was considered suitable for the reaction between Fe^{II} and 1,10-phenanthroline.[31] With these results, a buffer concentration of 0.20 mol L^{-1} was selected, which corresponded to the addition of 4 mL of a 0.50 mol L^{-1} acetate buffer solution (pH = 4.5) to the 10 mL reaction flask. Under this condition, the final pH of the solution was always around 4.0.

Optimization of the extraction conditions

After the initial conditions for the spectrophotometric determination of Fe in the aqueous medium were established, the optimization of the extraction conditions was started. In this case, the influence of different factors on the Fe extraction from diesel oil was studied. As mentioned in the experimental section, sample D_1 spiked with 1.0 mg L^{-1} of Fe (organometallic form) was used in these experiments.

Optimization of the HNO_3 concentration in the extractant solution

Other works[17,19,21-23] related to EIEB have demonstrated that the concentration of HNO_3 in the extractant solution plays a central role in the extraction process. It is well known that metallic cations are displaced from organic structures due to the action of H^+.[17] In turn, in the present work, the concentration of HNO_3 had to be carefully controlled since it had to be enough to promote the quantitative extraction of the analyte from the organic to the aqueous phase, but it could not be so high to impair the adjustment of the pH of the medium to a value suitable to conduct the colorimetric reaction. In this context, the concentration of HNO_3 in the extractant solution was evaluated in the range of 0.0 (no addition of HNO_3) to 7.0 mol L^{-1}. The concentration of Triton X-100® in the extractant solution was maintained at 2.5% (m/v), and the final buffer concentration (acetate buffer, pH = 4.5) in the medium where the colorimetric reaction took place was 0.20 mol L^{-1}. The concentrations of ascorbic acid and 1,10-phenanthroline were those previously optimized.

As displayed in Figure 2, initially, in the absence of HNO_3, the absorbance signal was practically null, indicating that Fe cannot be extracted to the aqueous phase without using HNO_3. This result reinforced the importance of H^+ in the extraction process. With the increase in the HNO_3 concentration in the extractant solution, the increase in the absorbance signal was verified as well as the occurrence of a plateau in the range of 1.4-4.2 mol L^{-1} HNO_3. Between these concentrations, the suitable extraction of Fe can probably be obtained without reducing the ability of the buffer to adjust the pH of the final solution for the reaction between Fe^{II} (obtained after the reduction of Fe^{III} by ascorbic acid) and 1,10-phenanthroline. On the other hand, when the HNO_3 concentration was higher than 4.2 mol L^{-1}, the absorbance signal decreased, certainly due to the insufficient concentration of buffer added to the extract, which remained excessively acidic to permit the

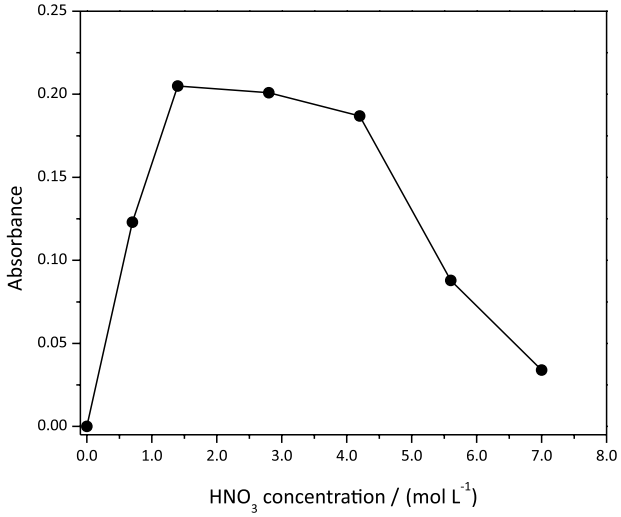

Figure 2. Influence of HNO_3 concentration in the extractant solution on the absorbance signal of the final solution used for the spectrophotometric determination of Fe.

colorimetric reaction. Therefore, in order to work under more robust conditions, an extractant solution containing 2.8 mol L^{-1} of HNO_3 was maintained for Fe extraction.

Optimization of the Triton X-100® concentration in the extractant solution

EIEB is based on the formation (and breakdown) of an emulsion between an aqueous solution (extractant solution) and an oil phase (organic sample). The convenient dispersion of one phase in the other depends on the addition of an emulsifying agent, which is, in most cases, a surfactant. In the present work, Triton X-100® was employed for this purpose, especially due to its good solubility in water and in oil. The concentration of the surfactant affects the stability of the emulsion formed by controlling the size of the droplets of the dispersed phase[33-35] and, consequently, the extraction efficiency since the preparation of emulsions with smaller droplets increases the interfacial area, thus improving the extraction efficiency. On the other hand, very stable emulsions are difficult to break, making the procedure laborious and time-consuming. Therefore, to reach a compromise between these two aspects, we studied the effect of the Triton X-100® concentration in the extractant solution. In this study, we varied the Triton X-100® concentration in the extractant solution between 0 (without surfactant) and 4.0% (m/v). The results are shown in Figure 3.

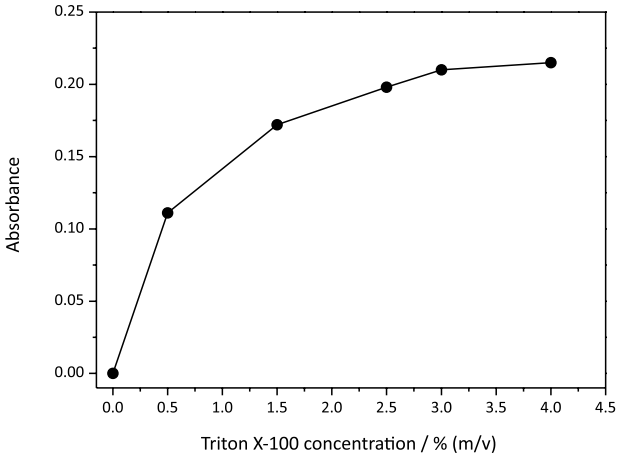

Figure 3. Influence of Triton X-100® concentration in the extractant solution on the absorbance signal of the final solution used for the spectrophotometric determination of Fe.

The obtained results showed that the surfactant concentration significantly influenced the extraction of Fe from diesel oil samples using the proposed strategy. Maximum absorbance was verified for the higher concentrations of Triton X-100® tested (between 3.0 and 4.0% (m/v)), which indicated that the extraction was dependent on the characteristics of the emulsions formed. In this case, enhanced extraction was observed when the stability of the emulsion was increased (smaller droplets), denoting that the interfacial area between aqueous and oil phases affects the extraction process.[33-35] Therefore, a Triton X-100® concentration of 3.0% (m/v) was selected for the extractant solution. On the other hand, the use of this concentration of surfactant presented a problem. The aqueous phase turned turbid after emulsion breakdown, probably due to the enhanced transference of organic matter to the aqueous phase. Spectrophotometric measurement of the turbid solutions was not possible because of the intense scattering of electromagnetic radiation observed under this condition and, to overcome this drawback, the solutions were always filtered through a 0.22 μm membrane, which was efficient to eliminate turbidity.

Evaluation of calibration conditions

One of the most challenging steps in the whole analytical process is the correct choice of the calibration approach. This aspect is particularly difficult when the samples are submitted to a previous treatment because the final medium where analytes are inserted must be reproduced in the standard solutions used in the calibration. Therefore, to verify if non-specific interferences would affect the proposed method, the calibration was tested using an analytical curve and a standard addition curve prepared by the addition of Fe^{III} to the extract obtained from the application of EIEB to sample D_1. Obviously, in both cases, the concentrations of the reagents were the same and equal to those optimized in the previous steps of this work.

The analytical curve presented a typical equation of $A = (0.210 \pm 0.001)\,[Fe(mg\,L^{-1})] + (0.0004 \pm 0.0011)$ (with a coefficient of determination, $r^2 = 0.999$), whereas the standard addition curve was $A = (0.212 \pm 0.005)\,[Fe(mg\,L^{-1})] + (0.0112 \pm 0.0052)$ ($r^2 = 0.998$). The sensitivities of both curves were not significantly different at 95% confidence level when a Student's *t*-test was used to compare the results. The value of *t* was 1.054, and the critical value was 2.306 (degrees of freedom = 8, two-tailed test), which indicated that calibration of the method could be securely performed using an analytical curve prepared in deionized water. These results also showed that the transference of organic material from the sample to the aqueous extract was very low (and efficiently removed by filtration) and did not change the final composition of the solution in a significant proportion to affect the spectrophotometric determination of Fe.

Figures of merit of the method

The limit of detection (LOD) and limit of quantification (LOQ) of the method were calculated using the analytical

Table 1. Comparison of different methods for Fe determination in diesel oil samples

Sample preparation approach	Analytical technique	LOD/LOQ	Reference
Diesel oil mineralization using an optimized method based on focused microwave irradiation	ICP OES	0.14 μg g^{-1}/ LOQ not reported	12
Extraction induced by emulsion breaking followed of GF AAS determination	GF AAS	183 ng L^{-1}/ 609 ng L^{-1}	17
Direct injection of samples diluted with xylene	ICP OES	2.27 and 1.73 μg g^{-1} [a]	37
Acid decomposition of samples in a closed-vessel microwave oven[b]	ICP-MS	1.28 μg g^{-1}/ LOQ not reported	38
Analyte extraction with diluted solutions of nitric acid using a counter current system	ICP-MS	0.1-3000 μg g^{-1} [c]	39
Extraction of iron by EIEB followed of spectrophotometric determination with 1,10-phenanthroline	spectrophotometry	0.004 mg L^{-1}/ 0.013 mg L^{-1}	this work

[a]These values correspond to BEC (background equivalent concentration) for different instruments; [b]in this work, the analyzed samples were fuel oils; [c]measuring range using the developed method. LOD: limit of detection; LOQ: limit of quantification; ICP OES: inductively coupled plasma optical emission spectrometry; GF AAS: graphite furnace atomic absorption spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; EIEB: extraction induced by emulsion breaking.

curve prepared in deionized water and the experimental conditions optimized for the generation of the colored product. They were obtained from 10 independent measurements of the blank and using 3.3σ and 10σ criteria,[36] respectively. It is important to note that the preconcentration/dilution factors involved in the procedure, which were related to the extraction (5× preconcentration) and measurement (20× dilution) steps, were considered. The quantitative transference of Fe from the sample to the aqueous extract was also considered. Under these conditions, the LOD for the method was 0.004 mg L^{-1} and the LOQ was 0.013 mg L^{-1}, and both were related to the concentration of Fe in the sample. Despite the use of a less sensitive analytical technique for Fe quantification in the samples, the LOD and LOQ observed for the developed method are comparable to those reported in other works devoted to the Fe determination in diesel oils (Table 1). The intermediary precision of the method was also estimated through the analysis of one sample (D_4) on three different days. The intermediary precision of the method was 8.0%.

Application of the proposed method

After its optimization and characterization, the proposed method was employed in the analysis of six samples of diesel oil, which were purchased from gas stations in the city of Niterói-RJ, Brazil. Among these samples, three were specified as S10 (maximum sulfur concentration of 10 mg kg^{-1}), and the other three were specified as S500 (maximum sulfur concentration of 500 mg kg^{-1}). The determination of Fe in the samples was performed by the proposed method using the optimized conditions established in previous experiments. The total Fe concentration was also determined by GF AAS in three samples using the reference method based on the injection of the samples in the form of emulsions, as in the work of Cassella *et al.*[32] The results are shown in Table 2.

Table 2. Results obtained in the determination of Fe in the samples of diesel oil by the proposed method and GF AAS. The results are expressed as mean ± standard deviation (n = 3)

Sample	Type	Fe concentration proposed method / (mg L^{-1})	Fe concentration reference GF AAS method[a] / (mg L^{-1})
D_1	S10	0.092 ± 0.011	0.095 ± 0.008 (t = 0.408)
D_2	S10	0.30 ± 0.02	n.d.
D_3	S10	0.21 ± 0.02	0.20 ± 0.03 (t = 0.306)
D_4	S500	0.65 ± 0.04	0.60 ± 0.02 (t = 1.75)
D_5	S500	0.57 ± 0.03	n.d.
D_6	S500	0.42 ± 0.04	n.d.

[a]The critical value of t in all cases was 2.776 (degrees of freedom = 4, two-tailed test); GF AAS: graphite furnace atomic absorption spectrometry; n.d.: not determined.

As can be seen in the results shown in Table 2, the concentration of Fe in all six samples was above the LOQ of the method, independent of the type of diesel oil analyzed, proving its applicability for the proposed task. Significant differences between the results obtained by the proposed method and the reference method were not observed, which indicated that the method was accurate for the determination of Fe in diesel oil. This comparison was carried out using the Student's t-test (at a 95% confidence level), and the values of t are also shown in Table 2. It is important to note that all variances were tested using the F-test, demonstrating that the average values were homoscedastic.

To confirm the accuracy of the proposed method, a recovery test was also performed with the six samples. In this test, each sample was spiked with 1.0 mg L^{-1} of

Fe in the form of an organometallic compound followed by the application of the optimized method (extraction and analysis). The recovery percentages were calculated by the difference between the Fe concentrations found in the spiked and non-spiked samples. The results obtained in the recovery test are shown in Table 3. As can be seen, the recovery percentages were suitable for quantitative purposes since the values were always situated between 83 and 108%.

Table 3. Results obtained in the recovery test applied to the samples. In all cases, the concentration of Fe added to the samples was 1.0 mg L^{-1}. The results are expressed as mean ± standard deviation (n = 3)

Sample	Type	Recovery / %
D_1	S10	108 ± 8
D_2	S10	83 ± 11
D_3	S10	90 ± 7
D_4	S500	93 ± 5
D_5	S500	89 ± 8
D_6	S500	93 ± 6

Conclusions

The method proposed in this work for the determination of Fe in diesel oil involved the use of a low-cost analytical technique (spectrophotometry with 1,10-phenanthroline as the chromogenic reagent) and was shown to be simple, reliable, and sensitive enough to quantify this metal in commercial samples. The application of the EIEB procedure allowed for the quantitative extraction of Fe from diesel oil, thus avoiding the necessity of mineralization of the samples before analyte measurement, making the entire analytical process faster and less risky for the analyst.

The main challenge faced during the development of the method was to adjust the pH of the final extract to allow the complexation reaction to take place in a suitable extension. For this purpose, an acetate buffer solution with a pH of 4.5 was employed because the final extract was excessively acidic. This work, in our opinion, opens a window for the development of novel applications of EIEB based on the low-cost spectrophotometric determination of other analytes in other types of samples.

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