

Analytical Methods

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A new procedure for on field and indirect photometric determination of water in ethanol fuel

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This technical note addresses the development of a simple, fast, portable, inexpensive, and indirect method for determination of water in ethanol fuel. The excessive addition of water is the most easy and usual adulteration way of these fuels, damaging the vehicle performance. The developed system relies on a homemade photometry device to monitor complexation reactions between ethanol and cerium (IV). Such reactions generate deep orange-red solutions. The parameters of limit of detection and analytical sensitivity were estimated to be 0.22% v/v (water in ethanol) and 0.11 (% v/v)⁻¹, respectively. The developed platform exhibited satisfactory robustness concerning the changes in temperature and storage stability of the reagents. Additionally, the measurements were accurate in relation to the data obtained by Karl Fisher titration at 95% confidence level.

Introduction

In recent years, the production of biofuels has been encouraged and promoted by public authorities to reduce the dependence on the petroleum and emission of greenhouse gas. Additional reasons include the oil depletion and energy security concerns.^{1,2} Ethanol is the most produced biofuel in the world, reaching approximately 90 billion liters in 2013.³ Such energy matrix is a great alternative in relation to the derivatives of the petroleum because it is achieved from renewable sources, including sugarcane, corn, wheat, beet, and cassava.^{4,5}

In Europe, USA, Brazil, and other countries such as Argentina, Japan, India, and Mexico, anhydrous ethanol is added in gasoline to improve the fuel performance by operating as octane booster.^{4,6} In Brazil, hydrous ethanol is used like fuel since 1975. Currently, the hydrated ethyl alcohol fuel (HEAF) is the second most consumed fuel (in volume) for transportation purpose owing to the growing sales of flexible fuel (flex-fuel) vehicles (FFVs).^{6,7}

Concerning the consumption of HEAFs, its adulteration by adding species that are foreign or above their permitted content has also increased.^{7,8} The most common and easy adulteration is the excessive addition of water in HEAF samples because the attained mixtures are colorless, visibly undetected, and do not present a distinctive smell.^{8,9} It can melt the heads of piston damaging the motor and generating a poor vehicle performance, including loss of engine power and increase in the fuel consumption rate.¹⁰

The maximum of water concentration in HEAF established by Brazilian regulatory agency (*Agência Nacional do Petróleo*, ANP) is 4.9% (v/v).¹¹ Herein, the major quantification techniques are: *i*) glass densimeter and *ii*) Karl-Fischer titration. Despite their high simplicity, the density measurements are not specific for water as well as their data can be easily masked by the addition of foreign species.^{4,12} The Karl-Fischer titration, in turn, has been used as a standard method because it enables simple measurement of water content with high accuracy, selectivity, and wide linear range.¹³ Nevertheless, this standard approach requires dedicated appliance and consumes a range of chemicals, yielding assays of high-cost and incompatible for *in-situ* monitoring.^{4,7} Consequently, several methods for the determination of water in HEAF were addressed in the

literature, including: *i*) near infrared spectrometry,^{9,13,14} *ii*) conductometry,⁴ *iii*) enthalpimetry,¹⁵ *iv*) cyclic voltammetry,¹⁶ *v*) photothermal detector,¹⁷ *vi*) ultrasonic propagation velocity,⁸ and *vii*) evanescent field absorption spectroscopy.¹⁸

Spectroscopy methods were also developed to evaluate water content in organic solvents such as biodiesel,¹⁹ acetone,²⁰ and fugacillin.²¹ In this paper, we report a new alternative for indirect determination of water in HEAF. The method relies on colorimetric complexation reactions between ethanol and cerium (IV) that generate deep orange-red solutions.²²⁻²⁴ The photometry is a potential approach because it needs a simple and portable instrumentation, as well as provides fast, selective, sensitive, and robust experiments.²⁵ Therefore, the method herein reported is promising for the development of rapid testing tools by compromising ease in prototyping, analytical performance, portability (key aspects in the research), low cost, and reliability in use (concerns in industry).

The following tests were included herein: *i*) optimization of the reagent concentrations, *ii*) evaluation of the method performance by obtaining analytical curves, *iii*) tests of stability of the complex formation and reagents, and *iv*) application to determine water in ethanol fuel samples.

Experimental methods

Chemicals and reagents

Ceric ammonium nitrate [(NH₄)₂Ce(NO₃)₆] was purchased from Vetec (Rio de Janeiro, Brazil). Nitric acid (HNO₃) and ethanol were supplied from Merck (Darmstadt, Germany). The chemicals were of analytical reagent grade. All of the solutions were freshly prepared using deionized water (Purelab, ELGA) with resistivity no less than 18 MΩ cm⁻¹.

Home-made photometry system

The components and assembled version of the photometric system are shown in Fig. 1. The device is composed by layers in acrylic mechanically connected. In addition, reservoirs, light source, and detector make up the platform. It allows automatically moving an acrylic piece (through a stepper motor) that presents reservoirs for the samples. It facilitates a vertical alignment between the solution, light source, and

1 detector improving the precision of the method. The reservoirs
 2 (reaction zones) were engraved on a dark acrylic piece (124 x
 3 21 x 4 mm) by using CO₂ laser with 1000 W power, 500 Hz
 4 frequency, 2000 mm min⁻¹ speed, and 0.1 mm spot beam size.
 5 Such piece contained six reservoirs (7 mm diameter and 4 mm
 6 deep) and it was fixed on a glass slide of 1 mm thickness
 7 (reservoir bottom) by employing adhesive. Electronics, in turn,
 8 was made according to the paper reported by Ellerbee *et al.*²⁶
 9 Its leading components are: *i*) RGB light-emitting diode (LED),
 10 *ii*) integrated switch to select a specific color, *iii*) photodiode (9
 11 mm² active area), and *iv*) filter tuned at 2 kHz to minimize the
 12 effects of the external light on the analyses. The electronic
 13 circuit is illustrated in Fig. S1 (Supplementary Information).
 14 The analytical responses are relative to the LED-emitted light
 15 that is converted in voltage signal by the photodiode. Analog-
 16 to-digital converter (National Instruments®, Austin, TX) was
 17 employed to transform the voltage analog signal in digital code.
 18 The system was controlled by Labview® (National
 19 Instruments®) software. A blue LED with wavelength of 470 ±
 20 10 nm was selected as light source. This fact provided the more
 21 sensible data because it corresponds approximately to the
 22 complementary color of the produced orange complex
 23 solutions.²⁷

27 Analytical routine

26 For indirect analysis of ethanol, a solution containing Ce(IV)
 27 and HNO₃ reagents was initially added to the reservoir. Then,
 28 ethanol aqueous solutions (standard or real sample) were
 29 prepared at concentrations from 0.2 up to 5.0% v/v were
 30 transferred with aid of micropipette. In both the cases, the
 31 introduced volume was 70 μL. Upon rapid mixture by using the
 32 micropipette tips, the reactions occur immediately with a color
 33 change from yellow to orange. The absorbance was calculated
 34 by using logarithmic ratios involving the peak heights obtained

35 in detector response for ethanol (H_{EtOH}) and blank (H_{blank})
 36 according to the Beer's Law:²⁶

$$37 \mathbf{A} = -\log \frac{H_{\text{EtOH}}}{H_{\text{blank}}} = \epsilon \mathbf{b} \mathbf{c} \quad (1)$$

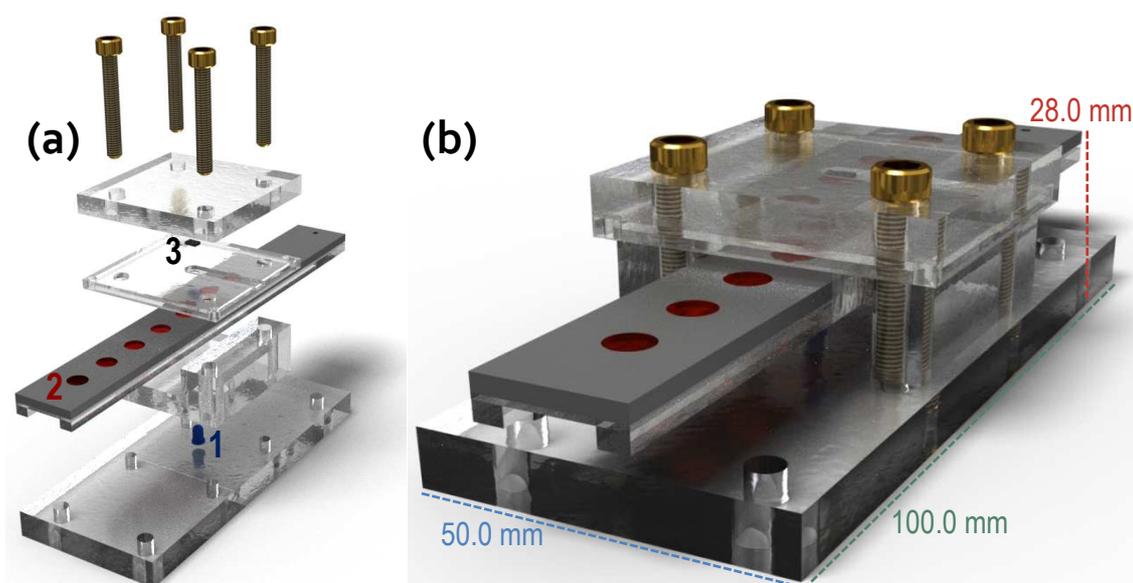
38 wherein \mathbf{A} is absorbance, ϵ is the molar absorptivity of the
 39 formed complex, \mathbf{b} is path length, and \mathbf{c} is the analyte
 40 concentration.

41 Optimization of the reagent concentrations

42 Different concentrations of the colorimetric reagents (Ce(IV)
 43 and HNO₃, see Table 1) were tested aiming to improve the
 44 detectability, sensitivity, and linearity. The pH of all these
 45 solutions was measured with values lower than 1. It is due to
 46 high HNO₃ concentrations. This investigation was performed
 47 taking into account the parameters: *i*) limit of detection (LOD);
 48 *ii*) analytical sensitivity (\mathbf{S}); *iii*) limit of linearity (LOL), and *iv*)
 49 correlation coefficient (\mathbf{R}^2). For this, analytical curves were
 50 attained for ethanol standards using all of the investigated
 51 conditions. Three measurements were conducted for each
 52 concentration of ethanol ($n = 3$). The signal/noise ratio method
 53 was adopted to calculate the LOD.

54 Stability of the complex and reagents

55 The ideal concentrations for the colorimetric reagents were
 56 used to test the produced complex stability after reaction with
 57 ethanol. For such, the intensity of color was monitored during
 58 three hours for solutions of 0.2, 0.6, and 1.0% v/v ethanol in
 59 water ($n = 3$). The analytical signals were recorded to each 5
 60 and 10 min up to 30 and, then, 180 min. Furthermore, the
 61 storage stability of the reagent solution (Ce(IV) and HNO₃) was
 62 tested. It was stored in three conditions, namely: room
 63 temperature (23 °C), refrigerated media (4 °C), and
 64 thermostatic bath (30 °C).
 65



57 Fig. 1 Home-made photometry system. Components of the developed platform (a) and the assembled device (b). 1, blue LED (light source); 2, sample
 58 reservoir (reaction zone); and 3, photodiode (detector). These three parts are vertically aligned. Features not drawn to scale.

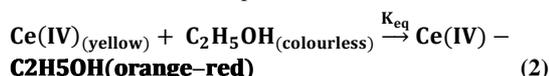
The photometry responses were achieved during 30 days for 0.6% v/v ethanol solution ($n = 3$).

Determination of water in HEAF

The indirect determination of water in ethanol fuel samples were made in order to assess the accuracy of the device herein reported. Real samples were acquired from distinct gas stations. All these samples were previously diluted 150 times with water and, then, analyzed by the photometric platform. Such dilution factor was considered to express the final content results. The water concentrations were compared to those recorded by Karl-Fischer titration (Metrohm, Titrand 890, Herisau, Switzerland), which acted as reference method. The latter is an official technique established by the ANP.¹¹ Three measurements for each sample were performed. Statistical evaluation between the data achieved by both the techniques was realized using Student's t-tests at 95% confidence level. Lastly, the conductivity values of the real samples were measured by using an AJ Micronal AJX-522 (São Paulo, Brazil) system.

The reaction

In this technical note, we address a simple platform to indirectly determine water contents in ethanol fuel. It is based on colorimetric reactions among Ce(IV) reagent and ethanol. Ce(IV) is a versatile single electron oxidant adopted for the oxidation of alcohols and α -hydroxy acids such as lactic, malic, and tartaric acids.^{22,28} It forms red complexes with compounds which contain alcoholic hydroxyl groups (-OH). When yellow ceric ammonium solutions are mixed with ethanol, a deep orange-red color immediately appears owing to formation of 1:1 Ce(IV)-ethanol complexes as follows:



According to Young and Trahanovsky,²⁹ ceric ammonium nitrate has six nitrate ions surround each Ce(IV) atom. The nitrates are coordinated to cerium in a bidentate fashion so that the cerium coordination number is 12. After adding ethanol, it replaces one of the Ce-O bonds producing monodentate nitrate. Therefore, the generated complex contains five bidentate nitrate groups with one monodentate nitrate group and one alcohol chain. More recently, Briois *et al.*²⁴ utilized time-resolved X-ray absorption spectroscopy combined with UV-Vis and Raman spectroscopies to research the complex structure. They confirm the 12-fold oxygen coordination sphere of the Ce(IV)-ethanol complex. Nonetheless, the number of bidentate nitrate groups were found to be only two instead of five. According these authors, the Ce(IV)-ethanol complex is stemming from nucleophilic substitution reactions of water by the alcohol.

Results and discussion

Optimization of the reagent concentrations

The influence of the concentrations of Ce(IV) complex and HNO₃ was investigated aiming to improve the signal/noise ratio

and, thus, to raise the sensitivity and detectability of the method. The studied conditions are shown in **Table 1**.

According to Pinyou *et al.*,²² the reagent solution must be acidified with HNO₃ concentrations above 0.2 mol L⁻¹ in order the formation of aqueous complexes (Ce(NO₃)_m(H₂O)ⁿ⁺) instead of species with hydroxide groups (Ce(NO₃)_m(OH)⁽ⁿ⁻¹⁾⁺). In the first situation, the nucleophilic reactions are easier than the second one, favoring the formation of Ce(IV)-ethanol complexes and improving the sensitivity for ethanol analysis.

Table 1 Analytical curve parameters for the different content conditions of the colorimetric reagents. Units: mol L⁻¹ for [Ce(IV)] and [HNO₃], % v/v for LOL and LOD, and (% v/v)⁻¹ for S

Condition	[Ce(IV)]	[HNO ₃]	R ²	LOL	LOD	S
A	0.4	0.4	0.9913	1.90	0.21	0.14
B	0.2	0.4	0.9928	2.40	0.20	0.12
C	0.2	0.2	0.9880	2.25	1.13	0.14
D	0.4	0.2	0.9656	2.25	0.21	0.21

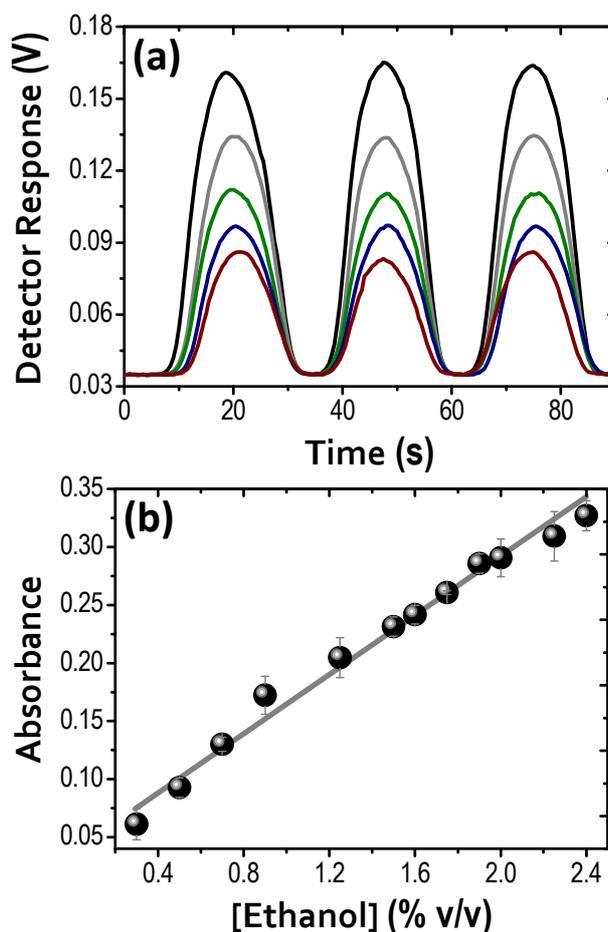


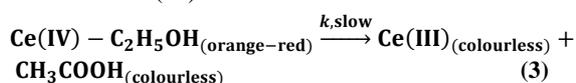
Fig. 2 Detector response obtained for ethanol solutions (a) and analytical curve ($n = 3$) for condition B (b). Ethanol concentrations in figure (A): 0.0 (—); 0.5 (—); 1.0 (—); 1.5 (—); and 2.0 % v/v ethanol in water (—).

The light transmitted through each reservoir results in a detector response as depicted in Fig. 2 A. Such profile is because the change in area of the sample that is exposed to photodiode (detection zone) when the acrylic piece is moved during the assay. The peak height corresponds to the middle of the reservoirs, where the detector is covering only the sample. The analytical signal was obtained from the peak height for analyte and blank according to the equation (1). The analytical parameters (R^2 , LOL, LOD, and S) recorded for each condition are presented in Table 1.

Conditions C and D generated non-linear data according to F-test.³⁰ Conversely, the linear fitting was validated for the other conditions. As expected, the poorer limit of detection was attained for C, where we have the lowest Ce(IV) and HNO₃ contents. Conditions A and B exhibited similar sensitivity and detectability. The latter was used for the next experiments due to its higher linear range. The analytical curve related to such condition is shown in Fig. 2 B. The other curves are depicted in Supplementary Information.

Stability of the complex formation and reagents

According to the articles published by Doyle²⁸ and Briois *et al.*,²⁴ the complex is not stable for long time. Alcohol in the 1:1 Ce(IV) complex is oxidized to aldehyde and, then, to carboxylic acid. The Ce(IV), in turn, is reduced to Ce(III) at room temperature as a slow electron transfer reaction like presented in equation (3). The rate constant, k , for Ce(IV) reduction is assumed to be dependent only on concentration of ethanol and Ce(IV).²⁸



The formation of the colourless Ce(III) was monitored during 180 min for three different ethanol concentrations as shown in Fig. 3.

The results were in agreement with the previous reports.^{24,28} For higher concentration of ethanol (1.0%), the Ce(III) formation was faster with respect to the lowest concentrations (0.2 and 0.6% v/v ethanol to water), taking into account the angular coefficients presented in Fig. 3 Inset. For 0.6 and 1.0% v/v, the response decreased linearly with time by approximately 60 min of reaction as illustrated in Fig. 3 Inset. In these concentrations, the absorbance decreased about 15% from five to ten minutes. However, the change in color was not measurable for 0.2% v/v until 25 min, then, the signals decreased until 60 min. After 60 min, the colors modified progressively towards yellow, and, then, colorless at 180 min. Negative signals were recorded owing to the formation of the colourless Ce(III). It produced $H_{\text{EtOH}} < H_{\text{blank}}$ generating a negative signal (see equation (1)). The colors of the solutions for 1.0% v/v ethanol are shown in Fig. 3 Inset; the results for other concentrations are in Supplementary Information. It should be noticed that the degradation of the Ce(IV)-ethanol complexes is not a drawback for analytical use of the method. This is because such approach involves rapid measurements which can be performed in less than five minutes.

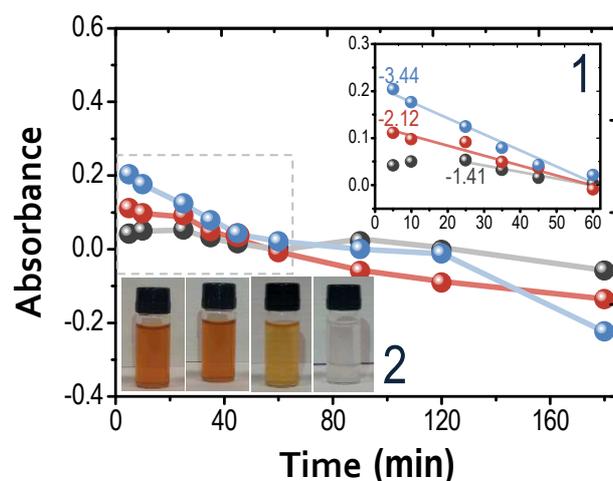


Fig. 3 Monitoring of the reaction during 180 min for three concentrations of ethanol: 0.2% (■), 0.6% (●) and 1.0% v/v ethanol to water (▲) ($n = 3$). Insets: 1, signals until 60 min (angular coefficients are highlighted) and 2, photos showing the formed complexes with 1.0% v/v ethanol to water after 0, 10, 60, and 180 min of reaction, respectively. R^2 values in Inset 1: 0.9786 (0.2%), 0.9749 (0.6%), and 0.9869 (1.0% v/v ethanol to water).

Regarding the storage stability test of the reagents, the absorbances obtained for ethanol 0.6% v/v for 30 days are shown in Fig. S4 (Supplementary Information). The RSD values of the responses were equal to 11.2 and 7.9 for reagents stored at 23 and 4 °C, respectively. The RSD for reagents stored at 30 °C was 5.9% in 15 days. After this period, the signal decreased with a RSD of 23.8%. These results show that the storage stability of the reagent (Ce(IV) and HNO₃) was good, in special when stored at refrigerator and at thermostatic bath by 15 days. Such data show that the method is potentially robust concerning the changes in temperature besides being simple and rapid. This is crucial, *e.g.*, for the development of point-of-use testing and commercial kits of the platform.

Application

The results of water concentration for standard and real samples are shown in Table 2. The latter presented a conductivity of 1.28 cm⁻¹, whereas it was only 0.37 μS cm⁻¹ for pure ethanol. Based on Student's t-tests at 95% confidence level, the data achieved by the colorimetric platform were in agreement with those recorded by the reference technique. Hence, we can state that there were not statistically significant differences between the data presented by Karl Fischer titration and the device herein reported despite the conductivity of the real samples and the dilution protocol. Analyses disclosed the presence of several ions in the samples, such as NO₃⁻, K⁺, Ca²⁺ (0.49 to 3.51 mg L⁻¹),³¹ Cu²⁺, Zn²⁺, Ni²⁺, and Fe³⁺ (8 to 57 mg L⁻¹).³²

In general, as observed in Table 3, our set up is a potential tool to analyze the adulteration of ethanol fuel by water considering, in special, parameters such as analytical frequency, portability, and cost. Besides the analysis of ethanol (analyte), the systems reported in literature can act by determining the concentration of water in the HEAF.

Table 2 Application of the device to H₂O level in ethanol (% v/v) determined by the Karl Fischer ($n = 4$) and photometric ($n = 3$) methods. Synthetic samples: **S**₁, 5.5%; **S**₂, 9.0%; and **S**₃, 17.0%; H₂O in ethanol. Real samples: **R**₁-**R**₃.

Samples	Karl-Fischer	Photometry
S ₁	5.2 ± 0.2	4.9 ± 0.5
S ₂	8.5 ± 0.1	8.9 ± 0.4
S ₃	17.2 ± 0.2	17.5 ± 0.9
R ₁	5.2 ± 0.2	5.6 ± 0.4
R ₂	5.0 ± 0.3	5.1 ± 0.2
R ₃	4.8 ± 0.2	5.0 ± 0.3

Other studies reported in literature describe the determination of water in organic media directly by spectrophotometry reactions.¹⁹⁻²¹ For instance, Pereira *et al.*¹⁹ determined water in biodiesel through color fading of the cobalt chlorocomplex. It generated a limit of detection for water, 2.5 10⁻⁴ % v/v with waste of 750 μL per determination. The waste produced by our method is only 140 μL per determination.

Conclusions

A simple, fast, portable, and inexpensive procedure was developed for determination of water contents in ethanol fuel. The method is a potential alternative for the development of *in-situ* analytical platforms, bypassing the necessity by either qualified operators or sophisticated equipments. Furthermore, the photometric platform provided precise, robust, and accurate data with reduced chemical consumption and satisfactory levels of detectability and sensitivity for determination of water in ethanol fuel. The results reported in this technical note had good robustness regarding the changes in temperature and storage stability of the reagents. Considering the growing demand for HEAF in countries like Brazil and USA, we believe the technology addressed herein is promising to determine the adulteration of these fuels by water. Lastly, the photometric system could be applied for other analytes and samples by just modifying the reagents.

Notes and references

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- † Electronic Supplementary Information (ESI) available: *i*) electronic circuit of the photometry system *ii*) analytical curves related to the investigated concentrations of Ce(IV) complex and HNO₃, *iii*) photos showing the colors of the solutions during the complexation reactions until 180 min and *vi*) results of storage stability test in three different temperatures.
- J. M. DeCicco, *Climatic Change*, 2012, **111**, 627.
 - E. Gnansounou, A. Dauriat, J. Villegas and L. Panichelli, *Bioresource Technol.*, 2009, **100**, 4919.
 - <http://ethanolrfa.org/pages/World-Fuel-Ethanol-Production>, accessed in April 2014.
 - M. S. Ribeiro, L. Angnes and F. R. P. Rocha, *J. Braz. Chem. Soc.*, 2013, **24**, 418.
 - H. S. P. Carneiro, A. R. B. Medeiros, F. C. C. Oliveira, G. H. M. Aguiar, J. C. Rubim and P. A. Z. Suarez, *Energ. Fuel.*, 2008, **22**, 2767.
 - L. C. Freitas and S. Kaneko, *Energ. Econ.*, 2011, **33**, 1146.
 - L. Bueno and T. R. L. C. Paixão, *Talanta*, 2011, **87**, 210.
 - M. K.-K. Figueiredo, R. P.B. Costa-Felix, L. E. Maggi, A. V. Alvarenga and G. A. Romeiro, *Fuel*, 2012, **91**, 209.
 - A. C. Silva, L. F. B. L. Ponte, M. F. Pimentel and M. J. C. Pontes, *Talanta*, 2012, **93**, 129.
 - <http://www.anp.gov.br/>, accessed in August 2013.
 - http://nxt.anp.gov.br/nxt/gateway.dll/leg/resolucoes_anp, accessed in June 2014.
 - <http://www.sindalcool.com.br/qualidade>, accessed in June 2014.
 - S. Cho, H. Chung, Y. Woo and H. Kim, *Bull. Korean Chem. Soc.*, 2005, **26**, 115.
 - R. Guchardi and C. Pasquini, *App. Spectrosc.*, 2001, **55**, 454.
 - W. A. de Oliveira and C. Pasquini, *Talanta* 1984, **31**, 82
 - P. F. Pereira, R. M. F. Sousa, R. A. A. Munoz and E. M. Richter, *Fuel*, 2013, **103**, 725.
 - C. R. Omido, S. L. Oliveira, R. S. Shiraishi, K. F. Magalhães, V. S. Ferreira, A. A. de Carvalho, C. Kitano and M. H. de Paula, *Sensor. Actuat. B-Chem.* 2013, **178**, 581.
 - F. B. Xiong and D. Sisler, *Opt. Commun.* 2010, **283**, 1326.
 - A. C. Pereira, B. F. Reis and F. R. P. Rocha, *Talanta*, 2015, **131**, 21.

Table 3 Comparison of analytical parameters reported for analysis of the ethanol fuel adulteration by water

Method	Analyte	LOD (% v/v)	LOL (% v/v)	Analytical frequency	Cost	Portability	Reference
Ultrasonic propagation velocity	Ethanol	N.I.	93.71†	Moderate	Medium	No	8
Cyclic voltammetry	-	0.028	0.500	Moderate	Medium	Yes	16
Colorimetry	-	0.2	2.4	High	Low	Yes	This work
Solubility difference of NaCl measured by conductivity	Water	0.05	16.00	Moderate	Low	Yes	4
Capacitive interdigitate sensor combined with chemometric treatment	-	7.5	25.0	Low	High	No	7
Miniaturized system in near-infrared	-	N.I.	19.0	High	Medium	Yes	13

N.I., non informed.

† from 89.84 to 93.71.

- 20 C. F. Matkovich and G. D. Christian, *Analytica Chimica Acta*, 1972, **60**, 319.
- 21 I. Kagevall, O. Aström and A. Cedergren, *Analytica Chimica Acta*, 1981, **132**, 215.
- 22 P. Pinyou, N. Youngvisees and J. Jakmune, *Talanta*, 2011, **84**, 745.
- 23 B. V. W. Reid and R. K. Truelove, *Analyst*, **1952**, **77**, 325.
- 24 V. Briois, D. Lützenkirchen-Hecht, F. Villain, E. Fonda, S. Belin, B. Griesebock and R. Frahm, *J. Phys. Chem. A*, 2005, **109**, 320.
- 25 Y. Suzuki, T. Aruga, H. Kuwahara, M. Kitamura, T. Kuwabara, S. Kawakubo and M. Iwatsuki, *Anal. Sci.*, 2004, **20**, 975.
- 26 A. K. Ellerbee, S.T. Phillips, A. C. Siegel, K. A. Mirica, A. W. Martinez, P. Striehl, N. Jain, M. Prentiss and G. M. Whitesides, *Anal. Chem.*, 2009, **81**, 8447.
- 27 D. C. Harris, *Quantitative Chemical Analysis*, 2010, 8th Edition W. H. Freeman and Company, New York.
- 28 M. P. J. Doyle, *Chem. Edu.*, 1974, **51**, 2.
- 29 L. B. Young and W. S. Trahanovsky, *J. Am. Chem. Soc.*, 1969, **91**, 5060.
- 30 F. A. L. Ribeiro, M. M. C. Ferreira, S. C. Morano, L. R. Silva, R. P. Schneider, *Quim. Nova*, 2008, **31**, 164.
- 31 R. A. A. Munoz, E. M. Richter, D. P. De Jesus, C. L. Do Lago, L. Angnes, *J. Braz. Chem. Soc.*, 2004, **15**, 523.
- 32 E. G. Vieira, I. V. Soares, N. L. Dias Filho, N. C. Da Silva, E. F. Garcia, A. C. Bastos, S. D. Perujo, T. T. Ferreira, A. H. Rosa, L. F. Faceto, *J. Colloid Interface Sci.*, 2013, **391**, 116.