



# Direct analysis of Cr, Ni, Pb and V in ethanol fuel by Microwave Plasma-Atomic Emission Spectrometry

## Application note

Energy and fuels

### Authors

George L. Donati\*, Renata S. Amais\*, Daniela Schiavo† and Joaquim A. Nóbrega\*

\* Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, SP, Brazil

† Agilent Technologies  
São Paulo, SP, Brazil



### Abstract

A simple dilute-and-shoot procedure for determination of Cr, Ni, Pb and V in ethanol fuel by Microwave Plasma-Atomic Emission Spectrometry (MP-AES) is proposed. Samples were easily prepared and neither special nor expensive gases were needed for performing analyses. All limits of detection from 0.3–40  $\mu\text{g/L}$  were compatible with the requirements taken into account when considering fuel impacts on environment and engine performance.



Agilent Technologies

## Introduction

Ethanol fuel has been commonly used in automobiles since the first petroleum crisis in the middle of the 1970s. More recently, the large number of flexfuel engines available, combined with the environmental advantages of using this renewable source of energy, have boosted the production and consumption of ethanol around the world. In Brazil, this fuel is produced from sugar cane, which provides high yields and is an example of a sustainable source of energy [1].

The presence of metals in fuels may reduce engine performance and/or deteriorate the quality of the fuel by oxidative decomposition reactions [2]. In addition, some potentially toxic elements can be naturally present in ethanol as a result of the soil composition where the sugar cane has grown. Alternatively, these elements can be introduced into the fuel during its production, storage and/or transport. Thus, after fuel combustion, these elements can significantly increase air pollution [3].

In this application note, we present the direct analysis of ethanol fuel for determination of Cr, Ni, Pb and V using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). This instrument is based on a nitrogen plasma, which is generated by magnetically-coupled microwave energy. One of its main advantages is the reduced costs of operation and maintenance. No separate gas source is required, since a nitrogen gas generator and a simple air compressor are sufficient to run the plasma. In this work, accurate results were obtained simply by diluting ethanol samples with 1% v/v HNO<sub>3</sub> aqueous solutions.

## Experimental

### Instrumentation

All measurements were carried out with the Agilent 4100 MP-AES. The sample introduction system was composed of solvent-resistant tubing, a double-pass cyclonic spray chamber and the inert OneNeb nebulizer. Because fuel samples were directly introduced with no previous treatment but dilution in aqueous solution, air was injected into the nitrogen plasma by an external gas control module (EGCM) to avoid carbon deposition on the torch or the pre-optics window. The injection of

air also contributed to maintaining the plasma stability and reducing background emission.

Background correction was performed automatically using the Auto Background Correction in the Agilent MP Expert software, which records, stores and subtracts the background spectrum for each element. The background spectrum is obtained from a blank solution. This spectrum is then subtracted from all reference and sample solutions. In addition, parameters such as nebulizer pressure and viewing position for each monitored wavelength can be automatically optimized. Tables 1 and 2 show the instrumental operating conditions and settings to determine Cr, Ni, Pb and V in ethanol fuel samples.

**Table 1.** Agilent 4100 MP-AES operating conditions for the direct analysis of ethanol fuel samples

Instrument parameter	Operating condition
Nebulizer	Inert OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	5
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

**Table 2.** Nebulizer pressures and EGCM settings for Cr, Ni, Pb and V measurements

Element	Wavelength (nm)	Nebulizer pressure (kPa)	EGCM*
Cr	425.433	240	High
Ni	352.454	180	High
Pb	405.781	100	High
V	437.923	240	High

### Reagents and standard solutions

Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) was used to prepare all solutions. Stock mono-element solutions containing 1000 mg/L of Cr, Ni, Pb or V (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions and to carry out spike experiments. Analytical grade ethanol (J. T. Baker, Hexis, São Paulo, SP, Brazil) was used to matrix-match the standard reference solutions used to build the analytical calibration curves.

### Samples and sample preparation

Ethanol fuel samples (hydrated ethanol) were obtained in local gas stations in São Carlos, SP, Brazil. According to the Brazilian legislation, the maximum allowable amount of water in hydrated ethanol fuel is 4.9% v/v [4]. Samples were diluted 10-fold in HNO<sub>3</sub> 1% v/v. Standard reference solutions used in the external calibration method were prepared by diluting adequate volumes of inorganic standard solutions of Cr, Ni, Pb or V in 1% v/v HNO<sub>3</sub>. Ethanol was also added to each standard reference solution to a final concentration of 10% v/v.

## Results and discussion

### Figures of merit

The analytical performance for each analyte was evaluated before the sample analysis. Limits of detection (LOD) and quantification (LOQ) were calculated by using the background equivalent concentrations (BEC), the signal-to-background ratios (SBR) and the relative standard deviations for 10 consecutive blank measurements in each case. Table 3 presents the LOD and LOQ values obtained. From these data one can notice the superior detection power of the 4100 MP-AES when compared to flame atomic absorption spectrometry (FAAS), for example. The microwave plasma is especially advantageous for refractory elements such as Cr and V. In this case, the higher temperatures reached in the plasma allow for lower LODs, with no addition of special gases as would be the case in FAAS determinations with nitrous oxide-acetylene flames [5].

To evaluate accuracy in direct analyses of ethanol fuel samples, spike experiments were performed with at least two different concentrations of each analyte added to the sample solution. Results are presented in Table 4. For all analytes evaluated, recoveries varied from 92 to 108% indicating low intensity of matrix effects commonly caused by organic compounds and concomitant elements such as Cu, Na, and Fe.

**Table 3.** Figures of merit for Cr, Ni, Pb and V determinations in ethanol fuel by MP-AES.

\* Instrumental limits of detection and quantification.

† Limit of detection considering sample dilution (1:9 v/v ethanol fuel in HNO<sub>3</sub> 1% v/v).

Element	LOD* (µg/L)	LOQ* (µg/L)	LOD in the sample† (µg/kg)
Cr	0.7	2.2	9
Ni	16	52	200
Pb	40	130	490
V	0.3	0.9	4

**Table 4.** Spike experiments for Cr, Ni, Pb and V determination in ethanol fuel samples

Element	Added (µg/L)	Found (µg/L)	Recovery (%)
Cr	20	21.2 ± 1.2	106
	100	95.1 ± 1.2	95
	500	460 ± 30	92
Ni	100	95.3 ± 0.8	95
	Pb	400	430 ± 10
1000		990 ± 10	99
V	20	19.8 ± 1.6	99
	100	98.4 ± 1.4	98
	500	460 ± 20	92

## Conclusions

The direct analysis of ethanol fuel samples using the Agilent 4100 MP-AES is a simple and effective method that can easily be implemented in routine analysis. Four samples were analyzed and none were contaminated. A simple dilute-and-shoot procedure, with solutions in 1% v/v HNO<sub>3</sub>, was adequate for accurate and precise determinations of Cr, Ni, Pb and V in ethanol. The EGCM prevented carbon deposition on the torch or on the pre-optical components and contributed to reduce the background signals and improve accuracy.

## Acknowledgments

The authors would like to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for scholarship and fellowship conceded to R.S.A. and G.L.D. (Grants 2010/17387-7 and 2010/50238-5, respectively). J.A.N. is thankful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). We also thank the technical support provided by Agilent Technologies.

## References

1. Silva, J. E., Silva, F. A., Pimentel, M. F., Honorato, R. S., Silva, V. L., Montenegro, M. C. B. S. M. & Araújo, A. N. (2006). A flow-batch internal standard procedure for iron determination in hydrated ethanol fuel by flame atomic absorption spectrometry. *Talanta*, *70*, 522–526.
2. Oliveira, M. F., Saczk, A. A., Okumura, L. L., Fernandes, A. P., Moraes, M. & Stradiotto, N. R. (2004). Simultaneous determination of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry using a glassy carbon-mercury film electrode. *Anal. Bioanal. Chem.*, *380*, 135–140.
3. Saint’Pierre, T. D., Maranhão, T. A., Frescura, V. L. A. & Curtius, A. J. (2005). The development of a method for the determination of trace elements in fuel alcohol by electrothermal vaporization - inductively coupled plasma mass spectrometry using external calibration. *Spectrochim. Acta Part B*, *60*, 605–613.
4. Brazilian National Agency of Petroleum, Natural Gas and Biofuels. Resolution ANP 7, D.O.U. 10.2.2011.
5. Amorim, F. A. C., Welz, B., Costa, A. C. S., Lepri, F. G., Vale, M. G. R. & Ferreira, S. L. C. F. (2007). Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. *Talanta*, *72*, 349–359.

[www.agilent.com/chem](http://www.agilent.com/chem)

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2012

Published August 3, 2012

Publication number: 5991-0771EN



**Agilent Technologies**