Analytica Chimica Acta 659 (2010) 15–22

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Analysis of fuels via easy ambient sonic-spray ionization mass spectrometry

Rosana M. Alberici[a,*], Rosineide C. Simas[a], Vanderléa de Souza[b], Gilberto F. de Sá[b,c], Romeu J. Daroda[b], Marcos N. Eberlin[a,b]

[a] ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, State University of Campinas, UNICAMP 13084-971, Campinas, SP, Brazil
[b] National Institute of Metrology, INMETRO, Division of Chemical Metrology 25250-020, Duque de Caxias, RJ, Brazil
[c] Federal University of Pernambuco, Department of Fundamental Chemistry, 50740-540, Recife, PE, Brazil

ARTICLE INFO

Article history:
Received 23 September 2009
Received in revised form
11 November 2009
Accepted 12 November 2009
Available online 18 November 2009

Keywords:
Ambient mass spectrometry
Easy ambient sonic-spray ionization
Fuel analysis
Quality control
Adulteration

ABSTRACT

The desorption and ionization of analytes directly from surfaces or natural matrices under ambient conditions has greatly simplified chemical analysis by mass spectrometry. Among the currently available set of such techniques, easy ambient sonic-spray ionization (EASI) is one of the simplest and most easily implemented. Fuels are among the most important and most complex classes of chemical mixtures and a challenge for fast and comprehensive chemical analysis. This review summarizes the applications of EASI-MS for fast, simple and nearly sample-preparation-free analysis of various fuels, focusing in typification, adulteration and quality control.

© 2009 Elsevier B.V. All rights reserved.

Contents

1. Chemical analysis of fuels

1.1. Gasoline

Automotive gasoline is a complex mixture of several hundred volatile and inflammable liquid petroleum-derived compounds

---

[*] Corresponding author. Tel.: +55 19 35213073; fax: +55 19 35213073.
E-mail address: rmalberici@hotmail.com (R.M. Alberici).

0003-2670/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2009.11.033

(mainly hydrocarbons) that range from four to twelve carbon atoms and have boiling points typically in the range of 30–225 °C. A great concern for gasoline quality control is the illicit addition of low quality solvents. Adulteration of gasoline with low-price materials or inappropriate solvents that will considerably alter the final properties of the fuel, such as octane number, is a common practice in many countries, and may cause environmental pollution, poor engine performance, and tax revenue losses [1]. Major gasoline adulterants are waste industrial solvents, mineral spirits, kerosene, rubber solvent, petrochemical light and heavy, diesel, paint thinner, and their mixtures. These include light aliphatic hydrocarbons (C4–C8), heavy aliphatic hydrocarbons (C13–C15) and aromatic hydrocarbons [2]. Because most solvents used in the adulteration are also petrochemical derivatives, the identification of their presence in gasoline is a challenging analytical task. Because the proper performance of gasoline as fuel depends upon a balanced combination of its constituents, a number of physicochemical tests such as relative density, temperatures equivalent to 10, 50, 90% of the distilled volume, final evaporation point, flash point, octane numbers (MON and RON), anti-knock indices values (AI), and benzene and sulfur percentages are currently applied to evaluate gasoline quality [3,4].

Recently, for instance, to control the illegal addition of solvents to gasoline, the Brazilian government has developed and implemented a program that determines the use of solvent markers to monitor their illegal admixture to gasoline [5]. However, this procedure is costly, highly demanding in terms of operational logistics and requires time-demanding analysis by GC–MS that only a few laboratories are able to perform. The development of improved analytical methodologies able to identify the presence of solvents in fuel and to certify origin and quality has therefore been the subject of extensive academic and forensic research. There are numerous reports on the gas chromatographic (GC) analysis of gasoline and related petroleum products [6–9]. GC has been used with flame ionization detection (FID) and mass spectrometry (MS) to evaluated modifications resulting from the addition of some solvents to gasoline [6]. Retention index databases and computer software are available from commercial sources for the detailed hydrocarbon analysis (DHA) of gasoline. However, the complexity of information obtained by GC makes the evaluation of the quality of gasoline by this technique difficult and tedious. Visual comparison of reference gasoline chromatograms to those of different gasoline samples is ineffective because changes in the oil feedstock, refining process and aging cause modifications in the chromatographic profiles of the gasoline, which do not necessarily mean quality deterioration. Multivariate analyses, such as principal component analysis (PCA), hierarchical clusters analysis (HCA) and linear discriminant analysis (LDA) of the gasoline, applied to data from GC, Fourier transform infrared spectroscopy (FTIR) [10], nuclear magnetic resonance (NMR) and other optical methods are important statistical tools to screen for gasoline adulteration by solvents [3–4,11], as well as to identify the origin of the gasoline [12], which is important information to determine the profile of fuel and to aid in the identification of dissimilar samples that may be associated with adulterations.

1.2. Biodiesel

Biodiesel is a renewable energy source of current worldwide interest and one of the most attractive alternatives for replacing the rapidly depleting and increasingly expensive petrofuels [13]. In contrast to petrofuels, which display quite standard compositions, biodiesel composition may however vary dramatically as a function of the various feedstocks used worldwide for their production. Biodiesel is mainly composed of a mixture of fatty acid mono-alkyl esters obtained from vegetable oils or animal fats. Trans-esterification is the most widespread process used to obtain biodiesel; it involves the catalyzed reaction of triglycerides (major compounds of oils and fats) and light alcohols (mainly methanol and eventually ethanol). Most industrial processes for trans-esterification employ alkaline catalysis (KOH, NaOH, or $NaOCH_3$). The designation of pure biodiesel is B100 (100% fatty acid alkyl esters). However, biodiesel is currently most often used in blends with fossil diesel and the Bn abbreviation will indicate the volume (in percent) of biodiesel in the mixture (for instance B3 is constituted of 3% biodiesel and 97% petrodiesel). In Brazil, B4 is currently mandatory and B5 will be mandatory in 2010 [14].

One of the main criteria for the quality of biodiesel is its storage stability (shelf-life). A relatively high degree of unsaturation of vegetable oils rich in unsaturated fatty acids makes their biodiesels susceptible to thermal and/or oxidative degradation/polymerization, which may form insoluble products that cause several problems within the fuel system, such as clogging at the injection pump [15,16]. For biodiesel standardization and quality control, most regulatory agencies require time-consuming measurements of several parameters via different techniques. In Brazil, the National Agency of Petroleum, Natural Gas and Biofuels (ANP) supplies the specifications of pure biodiesel and a number of methodologies for their characterization [14]. In fact, the Brazilian analyses are performed in accordance with the Brazilian Association of Technical Standards (ABNT), the standards of the American Society for Testing and Materials (ASTM) and the European Committee of Standardization (CEN) [17].

Biodiesel is commonly contaminated with residual glycerol (main co-product), tri-, di- and monoglycerides, alcohol and catalyst, as a result of incomplete reaction, as well as free fatty acids. These and other contaminants of biodiesel can lead to a number of operational and environmental problems such as corrosion and clogging. The most important quality parameters of biodiesel (contents of fatty mono-alkyl esters, fatty acids, glycerol and their acyl derivatives) are commonly determined by GC and high-performance liquid chromatography (HPLC). In fact, GC has been the most used technique due to its high accuracy for the quantification of minor components. However, baseline drift, overlapping signals, and aging of standards and samples can destructively affect GC accuracy [18]. Flame ionization detection (FID) is the most widespread detector used in GC analysis of biodiesels, but the use of GC coupled to mass spectrometer (GC–MS) has increased. GC–MS eliminates ambiguities in identifying eluting materials, but quantitation may be affected. HPLC analysis is less employed in biodiesel characterization, and the analysis time is normally longer than GC although sample derivatization is not required. Moreover, HPLC can be applied to biodiesel from different feedstocks and it is more appropriate for blend analysis than GC. Several detectors for HPLC biodiesel analysis are described, among them, evaporative light scattering detection (ELSD) is quite suitable. Spectroscopic analyses are most employed for monitoring the trans-esterification reaction and for the determination of blend levels (Bn). NMR and several techniques based on infrared spectroscopy (IR) are also commonly applied to these analyses [19–22].

1.3. Ambient mass spectrometry

Mass spectrometry has become an essential tool in science as a whole due to extraordinary advances and the great diversity and broadness of currently available ionization techniques. Electrospray ionization (ESI) mass spectrometry [23] and matrix-assisted laser desorption ionization (MALDI) mass spectrometry [24] are two of the most important examples of such advances since they have allowed the analysis of a much wider variety of analytes having various polarities and masses. But ESI and

Download English Version:

https://daneshyari.com/en/article/1167980

Download Persian Version:

https://daneshyari.com/article/1167980

Daneshyari.com