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Total reflection X-ray fluorescence as a convenient tool for determination of trace elements in microscale gasoline and diesel

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ABSTRACT

Quantitative determination of trace elements like S, Fe, Cu, Mn and Pb in gasoline and S in diesel is of great importance due to the growing concerns over air pollution, human health and engine failure caused by utilization of gasoline and diesel with these harmful elements. A method of total reflection X-ray fluorescence (TXRF) was developed to measure these harmful trace elements in gasoline and diesel. A variety of factors to affect measurement results, including TXRF parameters, microwave-assisted digestion conditions and internal standard element and its addition, were examined to optimize these experimental procedures. The hydrophobic treatment of the surface of quartz reflectors to support the analyte with neutral silicone solutions could prepare thin films of gasoline and diesel digestion solutions for subsequent TXRF analysis. The proposed method shows good potential and reliability to determine the content of harmful trace elements in gasoline and diesel with high sensitivity and accuracy without drawing different standard calibration curves, and can be easily employed to screen gasoline and diesel in routine quality control and assurance.

1. Introduction

The utilization of fossil fuels such as gasoline and diesel has been largely limited due to the negative effects of harmful elements in them. Sulphur dioxide (SO_2), one of major atmospheric pollutants, is responsible for acid rain, some human respiratory diseases and so on. While SO_2 is mainly attributed to combustion of sulphur-containing fuels, legal limit of sulphur in gasoline and diesel has been regulated in many countries down to 10–50 mg/kg or even less [1]. Nowadays, gasoline and diesel claimed “sulphur-free”, with sulphur content <10 mg/kg, are commercially available. However, the claimed content needs to be confirmed by an effective and generally accepted technique. Metallic elements are another issue in fossil materials and petroleum products. Metal elements such as Fe, Cu, Pb and Mn in gasoline catalyze the oxidation reaction of hydrocarbon compounds and/or the formation of gums, which can lower the quality of gasoline [2,3]. Among these metallic elements, Fe and Cu could make vehicle engines less efficient. The presence of Pb in gasoline can decrease the efficiency of catalytic converters and thus increase the emission of exhaust gases like CO_X, NO_x and SO_X, which greatly threaten human health. Thus, the contents of these four metallic elements in gasoline have also been regulated in some countries. In China, the legal limit of Fe, Cu, Pb and Mn in gasoline is in the range of 1–10 mg/L. To meet such regulatory limitations, fast, sensitive, accurate and reliable analytical methods and modern instrumentations are urgently needed [4].

Common techniques for determination of elements in gasoline and diesel include atomic absorption spectroscopy (AAS) [5–7], ultraviolet fluorescence (UF) [8–10], X-ray fluorescence spectrometry (XRF) [9, 11,12], inductively coupled plasma mass spectrometry (ICP-MS) [1, 13–15], inductively coupled plasma optical emission spectrometry (ICP-OES) [16–19] and isotope dilution mass spectrometry (ID-MS) [13]. ICP-MS and ICP-OES need to be tuned by various multi-element standard stock solutions before sample analyses and their results are largely affected by complex matrix effects. Additionally, various standard calibration curves are necessary for concentration determination. ID-MS is undoubtedly a highly accurate chemical analytical method and considered as one of primary measurement methods by some international organizations [1,20–23]. Isotope ratios instead of ion intensities are measured, which minimize the analyte amount without influencing the accuracy of measurement results. Therefore, this method is regarded as the certification method by most national metrology institutions for certified reference materials (CRMs) including petroleum products. Nevertheless, the high cost (instruments and isotope spikes) and the complex experimental process make it difficult to be employed for routine analysis. XRF, generally wavelength dispersive XRF (WD-XRF), has also been used as a standard and popular technique for determination of trace elements in petrochemical products. However,

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conventional XRF suffers from high background noises and strong matrix effects. Additionally, pre-treatment process is usually complex and needless.

The applications of total reflection X-ray fluorescence spectroscopy (TXRF) are very different from those of conventional XRF. TXRF provides a unique method for concentration determination. Compared with concentration XRF, the LOD of TXRF is significantly improved due to decreased matrix effects and increased signal-to-noise ratios [24–26]. In terms of sample preparation and analytical capability, TXRF has more in common with AAS, ICP-MS and ICP-OES [27]. On the aspect of samples, smooth thin films on sample reflectors are required. The samples such as oils and greases have already been detected by TXRF [28,29]. However, to the author's knowledge, studies were rarely published about the determination of trace elements in gasoline and diesel with TXRF [30]. To screen gasoline and diesel with harmful elements, TXRF may be a time-saving and cost-efficient technique capable of analyzing a very small amount of samples, and the quantitative results can be obtained by adding internal standard elements without drawing standard calibration curves.

The microwave-induced combustion (MIC) can provide a simple and rapid pre-treatment for some organic samples [31,32], but this method is not suitable for sample with high flammability and volatility for safety considerations. Moreover, MIC pre-treatment usually can't be carried out for most of microwave-assisted digestion (MWAD) systems, which greatly restricts its application. MWAD is often regarded as one of the most efficient ways for pre-treatment of samples, which makes samples react rapidly with acids [33]. This technique has been reported not only to promote the movement of ions, but also decrease the activation energy of the reactants [34]. The MWAD could be used for almost all types of samples if the conditions of MWAD were properly set. Herein, MWAD was used to digest gasoline and diesel samples. Bubbles in gasoline and diesel samples generated when nitric acid and hydrogen peroxide were added should be rested until disappear before the digestion vessel is transferred into the MWAD system for safety considerations. The simulated gasoline and diesel meeting national limitation regulations were used to optimize the MWAD procedures, and the gasoline and diesel CRMs of ERM-EF211 and ERM-EF673a from IRMM and LGC were utilized in order to validate the developed methods.

In this paper, a sensitive, accurate and reliable TXRF analytical approach is described to determine harmful trace elements of S, Fe, Mn, Cu and Pb in gasoline and S in diesel to meet the requirement within national limitation standards. An internal standard element is distinctively added to the analyte of gasoline or diesel before MWAD. With the use of internal standard element, the slight loss of samples in the process of MWAD and subsequent treatments should not influence the final analytical results. And it is not necessary to accurately measure volume or weight of sample in the final amount of concentrated digestion solutions, which is usually about dozens of microliters. Additionally, the operating conditions of MWAD and TXRF are evaluated systematically. It is shown that hydrophobic treatment of sample reflectors to support the analyte with neutral silicone solutions can prepare thin films of gasoline and diesel digestion solutions for TXRF analysis. As a comparison, ICP-OES is employed to measure target elements in gasoline and diesel. And consistent results demonstrate that TXRF is a promising technique for the analysis of gasoline and diesel samples.

2. Experimental

2.1. Instruments

TXRF analysis was performed using a benchtop NANOHUNTER ED-TXRF system (Rigaku, Japan) equipped with two air-cooled X-ray tubes, Mo and Cu anodes, and a semiconductor detector. The X-ray generator was operated at 50 kV and 0.8 mA for both anodes. The energy resolution of the instrument was 150 eV when multi-element standard was detected. Quartz reflectors were used as sample carriers. Sample carriers were rinsed with absolute ethyl alcohol for 20 min followed by 10 wt% nitric acid for 2 h prior to experimental performance. For TXRF measurements, the X-ray incidence angle of 0.10° and measurement time of 100 s were used for Cu anode, and the X-ray incidence angle of 0.05° and measurement time of 200 s were selected for Mo anode. An X-ray Cu anode was used for S, Fe and Mn elements and an X-ray Mo anode was used for Cu and Pb elements. A RS-P1100 vacuum dryer (Rigaku, Japan) was used to dry the digested samples dropped on the surface of quartz reflectors.

The ICP-OES analysis was performed using an iCAP7400 instrument (Thermo Fisher Scientific, USA) with an echelle optical design and a charge injection device (CID) solid-state detector to measure trace elements in gasoline and diesel samples. The sample introduction, RF generator, plasma and spectrometer were controlled using iTEVA software. Flow rates of auxiliary Ar gas, nebulizer Ar gas and coolant Ar gas are 0.6 L/min, 0.7 L/min and 12 L/min, respectively. For ICP-OES measurements, the characteristic spectral lines of 180.731 nm, 259.940 nm, 220.353 nm, 257.610 nm and 327.369 nm were selected for the determination of S, Fe, Pb, Mn and Cu, respectively.

A Multiwave PRO MWAD system (Anton Paar, AUT) equipped with up to eight high pressure quartz vessels with an internal volume of 80 mL was used for gasoline and diesel digestion to prepare samples for TXRF analysis. The maximum operating pressure and temperature were 80 bar and 280 °C, respectively. Pressure and temperature were monitored by the original sensors of the equipment.

The DSA100 drop shape analyzer (Krüss, GER) was used to detect the contact angle, which was used for in-detail study of TXRF sample droplets pipetted onto the sample reflector. Up to 8 droplets of samples were tested to ensure measurement accuracy of contact angle.

2.2. Samples, reagents and standards

Sulphur-containing gasoline and diesel CRMs (ERM-EF211 and ERM-EF673a) were purchased from Institute for Reference Materials and Measurements (IRMM) and Laboratory of the Government Chemist (LGC) for method validation. Simulated gasoline and diesel were prepared by adding single element stock oils into blank oils by gravimetric and/or volumetric methods. Sulphur-free isooctane and 2# diesel were used as blank oils, which were bought from Victoria Hailey Group company (VHG). Single element stock oils (1000 mg/kg ± 1 mg/kg) were purchased from VHG as well. According to national limitation standards, simulated gasoline is prepared as the isooctane sample containing S of 10 or 50 mg/kg, Fe of 10 mg/L, Pb of 5 mg/L, Mn of 2 or 8 mg/L and Cu of 1 mg/L. The simulated diesel is diesel sample containing S of 10 or 50 mg/kg. The results for S, Fe, Mn, Cu and Pb in gasoline and S in diesel obtained by TXRF and ICP-OES techniques were used to evaluate the recovery of the method.

Ultrapure water with resistivity of 18.2 MΩ cm was available from a Milli-Q integral water purification system (Millipore, US) and it was used in the whole experimental process of sample preparation and pretreatment to avoid contamination errors. A sub-boiling distillation system (CEM, US) was used for the purification of the concentrated nitric acid (Sinopharm Chemical Reagent Co., Ltd., CN) which was used in the process of MAWD. The concentrated nitric acid was also used to clean sample vessels before and after each MAWD. Hydrogen peroxide solution with 30 wt% H_2O_2 (Merck, DE) was also used to digest gasoline and diesel by MWAD method. The quartz and PTFE beakers as well as PP flasks were soaked in 10 wt% HNO_3 solution for 48 h to remove remaining trace impurities. Argon gas with a purity of 99.996 wt% was used for ICP-OES analysis. Neutral silicone (Pattex, DE) was used to coat quartz reflectors to obtain a hydrophobic surface before dropping test samples on it. Petroleum ether (AR) was used as organic solvents to solubilize neutral silicone. For elemental determinations, the working reference solutions for S determination were prepared by serial dilution of SRM 3154 containing S element of 10.3 mg/g ± 0.03 mg/g (National Institute of Standards and Technology (NIST), US). The working reference