Short communication

Sensitivity improvement in ICP MS analysis of fuels and light petroleum matrices using a microflow nebulizer and heated spray chamber sample introduction

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ABSTRACT

Reasons for signal suppression during the analysis of light petroleum matrices by inductively coupled plasma mass spectrometry (ICP MS) were examined. A decrease of the ionization efficiency of the plasma was found to be the principal factor responsible for this loss of sensitivity. Consequently, an interface based on a total consumption micronebulizer and a heated spray chamber was constructed to alleviate this problem. A method based on flow-injection ICP MS using this interface was developed for the direct multielement analysis of undiluted fuels (gasoline, kerosene) and gas condensates offering an increase in sensitivity by at least a factor of 3–4 in comparison with the existing setups.

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1. Introduction

Light petroleum matrices and refining products, such as gas condensates and fuels (gasoline or kerosene) contain several metals, including mercury [1–4], arsenic [5,6] or lead [7,8] present in the $\mu g\,kg^{-1}$ range. Their analysis is important in the different sectors of economy from refining to environmental risk assessment. Mercury or arsenic, identified as the major metals present in natural gas and gas condensates, are responsible for catalyst poisoning, fouling and corrosion of refining installations. Lead and manganese have been of interest because of their use in additives to improve the antiknock properties of gasoline [7–9].

A number of techniques have been developed for the metal determination in fuels and related petroleum samples [10,11]. They include graphite-furnace atomic absorption spectrometry (GF-AAS) [12–14], inductively coupled plasma atomic emission spectrometry (ICP-AES) [10,15], and, more recently, ICP-MS [10,16–18]. The latter is particularly attractive because of its capacity of the simultaneous multielemental analysis and the sub-$\mu g\,kg^{-1}$ limits of detection (LOD) theoretically allowing the direct analysis. However, the introduction of organic, especially oxygen-free, solvents in ICP-MS is known to be affected by plasma quenching and matrix effects [19]. Therefore, petroleum matrices were usually analysed after digestion [20] or considerable dilution [17,20].

Recent advances in ICP MS analysis of organic solvents were based on the reduction of the amount of solvent arriving at the plasma by lowering the uptake rate and desolvation as well as on operating the plasma at higher power levels. The use of conventional micronebulizers (100–300 $\mu l\,min^{-1}$) equipped with a low-volume spray chamber limits the risk of memory effects and allows an increase in sample throughput [21]. The use of conventional (double-pass Scott) spray chamber results in a low fraction of sample introduced into the plasma and can cause analyte fractionation. An interesting alternative is the use of direct injection nebulizers, such as the DIN (not commercially available anymore) and the DIHEN (direct injection high efficiency nebulizer) [18,22,23] because of a low internal dead volume, rapid response time, reduced memory effects, absence of analyte loss and the elimination of the problem of fractionation in the spray chamber. However, routine analyses of petroleum matrices with DIHEN have not been demonstrated, likely because of plasma perturbation, clogging and instability in time.

In our former works [4,21] an interface was developed, based on a total consumption micronebulizer for the introduction of xylene solutions into ICP MS. The increase in the nebulizer capillary diameter and the elimination of the internal connections has limited the problem of clogging, pressure instability and memory effects [24].

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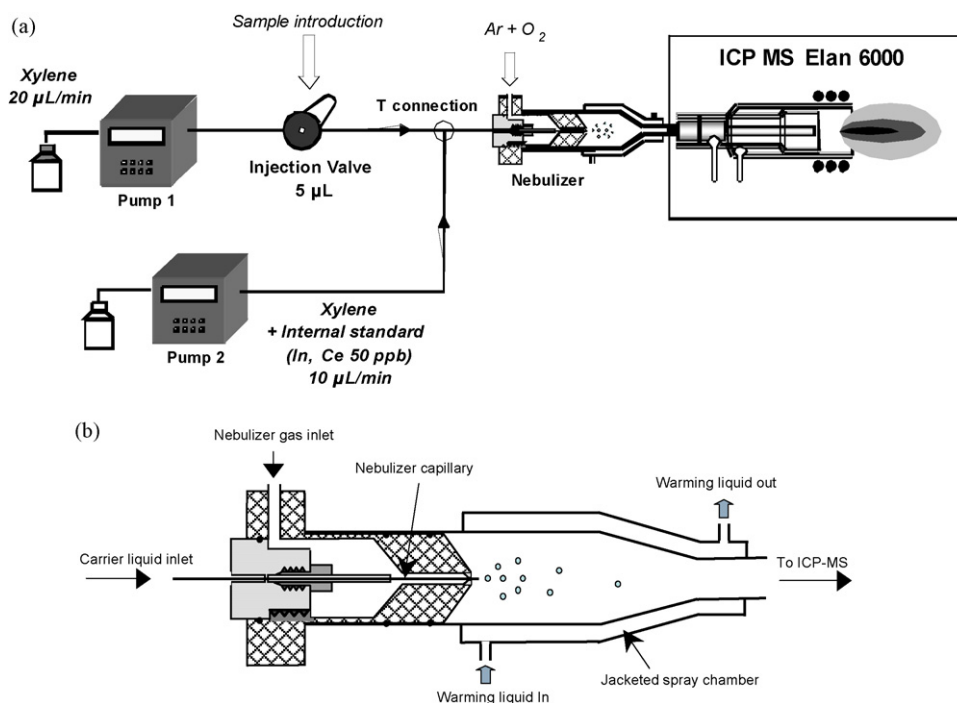E-mail address: brice.bouyssiere@univ-pau.fr (B. Bouyssiere).

Fig. 1. (a) Scheme of the analytical setup used. (b) Blowup of the sample introduction system.

However, the introduction of light petroleum fractions (gasoline, naphta) using this interface resulted in a significant plasma perturbation and, consequently, required dilution of the sample. This negatively affected the detection limits and was unsuitable for the analysis of trace elements (<0.1 mg kg^{-1}).

The purpose of this study was to examine the reasons for this loss of sensitivity and to propose sample nebulization into a heated drain-free spray chamber to reduce the perturbation of plasma and to increase the sensitivity of the analysis. This setup is the origin of an analytical method allowing the multielement analysis of fuels without dilution resulting in the detection limits at the 1 µg kg^{-1} level (gain of a factor 3–4).

2. Experimental

2.1. Apparatus

The ICP MS instrument used was a PerkinElmer Elan 6000 (PE-SCIEX, ON, Canada). The ICP AES was a Spectro Arcos (Kleeve, Germany) with radial viewing. The analytical setup is shown in Fig. 1a. A dual syringe pump (Model 140C, Applied Biosystems, Foster City, CA, USA) was used to assure a stable delivery of xylene into the ICP at a flow rate of 20 µl min^{-1} without the use of a splitter to limit the solvent consumption. Another pump (Smartline Pump 1000, Knauer, Berlin, Germany) was used to deliver internal standard (In, Ce) in xylene to the nebulizer to control the stability of the instrument. Injections were made using a low port-to-port dead volume micro-injection valve (8125i, Rheodyne, Rohnert Park, CA, USA) fitted with a 5 µl sample loop. The fused silica capillary used was 180 µm i.d. (375 µm o.d.). The sample introduction system was based on a microflow total consumption nebulizer described elsewhere [21]. The spray chamber was jacketed to allow the thermostating at a desired temperature (Fig. 1b). The heating liquid (glycol/water) was circulated through a Neslab RTE–111 (Thermo Fisher Scientific, Waltham, MA) thermostat. For ICP MS analysis, oxygen gas flow, controlled by a mass flow controller, was mixed with the carrier argon nebulizer gas via a T-connection prior to

nebulization, to prevent carbon deposition on the sampler and skimmer cones of the instrument. Oxygen was not needed for ICP AES analysis.

2.2. Samples and solutions

Alkanes (pentane, hexane, heptane, octane, decane, dodecane and hexadecane) were purchased from Acros (Acros Organics, NJ) and xylene (ACS grade) was purchased from Baker (Phillipsburg, NJ). Conostans monoelemental standards in oil (1000 mg kg^{-1}) and multielemental S-21 oil standard (100 mg kg^{-1}) were purchased from SCP Science (Baie D'Urfé, Canada). The standard reference material (CRM) crude oil 1634c was purchased from NIST (Gaithersburg, MD). Petroleum samples with different boiling range were provided by the French Institute of Petroleum (IFP-Lyon, France). They were kerosene (IBP = 162 °C and FBP = 252 °C), gasoline (IBP = 0 °C and FBP = 197 °C) and full range gas condensate (IBP = −25° and FBP = 470 °C) (IBP – initial boiling point; FBP – final boiling point).

2.3. Procedure

The ICP MS conditions were optimized daily using a solution of 50 µg kg^{-1} indium and cerium in xylene. The typical settings are RF power 1300 W, Ar nebulizer gas 0.8 l min^{-1}, and auxiliary O$_2$ flow 45 ml min^{-1}. The sample (5 µl) was injected into the carrier xylene at 20 µL min^{-1} and was mixed before the nebulizer with another xylene flow of 10 µl min^{-1} containing 50 µg kg^{-1} indium and cerium (internal standards) (Fig. 1a). Molybdenum was added at 50 µg kg^{-1} in each matrix analyzed to monitor the ionization efficiency. The isotopes measured in light petroleum matrices were ^{48}Ti, ^{51}V, ^{57}Fe, ^{107}Ag, ^{112}Cd, ^{114}Cd, ^{202}Hg, ^{208}Pb, and ^{53}Cr. ^{98}Mo was measured as a spiked analyte, ^{114}In as the internal standard and ^{58}Ni was measured in the CRM 1634c. The integration time per isotope was 20 ms, three readings were made per analysis, and each injection was made in triplicate. Quantification was made by the method of standard additions using the