



Determination of mercury in naphtha and petroleum condensate by photochemical vapor generation atomic absorption spectrometry[☆]

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ABSTRACT

In this work the feasibility of mercury determination in naphtha and petroleum condensate by photochemical vapor generation was investigated. The samples were pumped through the photochemical reactor as microemulsions and the volatile compounds formed were conducted to a quartz cell for the atomic absorption measurements. All the parameters of the system (sample preparation, organic precursor, sample flow rate, carrier gas flow rate and evaluation of the signal measurement mode) were investigated. The microemulsions were prepared mixing the samples with propan-1-ol and a small amount of water. The addition of low molecular weight organic acid was investigated and it was found not necessary once the propan-1-ol itself was efficient for promoting the generation of the volatile compounds of mercury. Calibration curves obtained with organic and inorganic standards showed correlation coefficients higher than 0.99 and characteristic mass of 2.0 and 2.4 ng of mercury for organic and inorganic standards, respectively, was obtained. There was no significant difference between the sensitivity of inorganic or organic standards for the calibration. Relative standard deviations ranged from 1 to 5% for three consecutive measurements. The limit of detection of $0.6 \mu\text{g L}^{-1}$, calculated for the amount of sample used in the microemulsion (1.0 mL), was obtained. A sample throughput was 2 samples per hour, considering triplicate analysis. Different naphtha and petroleum condensate samples were analyzed. No mercury was found in the naphtha samples, considering the limit of detection. In the petroleum condensate samples the concentrations ranged from 76 to $105 \mu\text{g L}^{-1}$. The accuracy was evaluated by assessing the recoveries of inorganic and organic species of mercury added to the samples, being obtained values in the range of 92 to 113%. The developed method was simple and fast, allowed direct analysis of naphtha and petroleum condensate with a reduced amount of reagents, thus contributing to green chemistry.

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1. Introduction

Naphtha and petroleum condensate are derived products from crude oil and they are important raw materials for the petrochemical industry. Naphtha is a very important feedstock for the fine chemical industries, used in gasoline formulation and in the production of ethylene, propene, benzene, toluene and xylenes [1]. Petroleum condensate replaces naphtha as raw material in the petrochemical industry; it is a heavier fraction of petroleum compared to naphtha and may contain higher concentration of metals [2]. The presence of trace elements, even in $\mu\text{g L}^{-1}$, in these petroleum-derived products can be associated

with many distinct problems such as: catalyzation of oxidative reactions, leading to a loss of the thermal stability of the products; release of some elements to the atmosphere in the refining process; corrosion problems and catalyst poisoning (in the case of naphtha); and also the presence of toxic elements remained in the distilled fractions, can be released to the environment when they are used as energy source [3,4].

Mercury is a trace component of all fossil fuels including natural gas, gas condensates, crude oil, coal, tar sands and other bitumens. The use of fossil hydrocarbons as fuels provides the main opportunity for emissions of the Hg they contain to the atmospheric environment [5,6]. Mercury is also a particular problem in the processing since it reacts with metallic surfaces causing corrosion and is a poison for noble metal catalyst used in many hydrocarbon process reactions. Many operators set tight limits on the level of Hg in naphtha feed to crackers (typically less than $5 \mu\text{g L}^{-1}$) [7]. Thus monitoring the presence of Hg in these products is increasingly demanded.

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The main problems of the determination of Hg in these samples are the fact that they are very complex and Hg is found in very low levels, requiring the use of highly sensitive techniques. There are few works in the literature concerning Hg determination in these samples. The direct analysis of naphtha and petroleum condensate after dilution of the samples with xylene by ICP-MS was proposed by Olsen et al. [8]. These authors reported that samples could be analyzed directly without pretreatment and the elements were determined simultaneously. However the standard deviation for Hg was very high, probably due to the instability of this element in organic solvent and possibly some memory effects. The emulsification of the samples with Triton X-100 was also proposed: it was reported that with the formation of emulsions a stability of at least one hour was obtained [9]. With the use of GF AAS, which is a technique adequate for complex matrices, and using Pd solution as chemical modifier, Santos et al. [10] used detergentless microemulsion as sample preparation and pre-concentrated Hg by multiple injections in the graphite tube obtaining a limit of detection of $0.78 \mu\text{g L}^{-1}$. Ceccarelli et al. [11] analyzed naphtha samples directly in the graphite tube for Hg determination obtaining a limit of detection of $32 \mu\text{g kg}^{-1}$.

The formation and analysis of emulsions or microemulsions have been successfully applied for the preparation of oil samples, due to the homogeneous dispersion and stabilization of the oil microdroplets in the aqueous phase, which brings the viscosity close to that of an aqueous solution and reduces the organic load of the system. Besides, it allows the use of aqueous standards for calibration instead of expensive and instable organometallic standards. This technique has been applied for determination of other elements in petroleum derivatives, as naphtha and petroleum condensate [1,3,12–14].

The use of methods based on vapor generation as sample introduction can offer important advantages for analysis of complex matrices, such as petroleum derivatives. With the previous separation between the analyte and the matrix and efficiency in sample introduction, great improvement in the limit of detection can be achieved and some serious spectroscopic and/or matrix interferences eliminated [15]. The main vapor generation methods (as cold vapor and hydride generation) normally make use of expensive and instable reagents, as tetrahydroborate (NaBH_4). Other disadvantages are that few elements can be converted to volatile compounds, the presence of transition metals (as Ni, Co and Cu) can cause the decomposition of the analyte hydride and the main reductor used, NaBH_4 , is a potential source of contamination [16]. Besides, the complete digestion of these organic samples is frequently required. There are a few works about determination of Hg in petroleum derivatives (gasoline samples) using chemical vapor generation without digestion procedures [17,18]. Due to all the aspects cited the development of alternative vapor generation systems for the determination of trace elements in complex samples is still necessary in atomic spectrometry.

An alternative method based on photochemical vapor generation (PVG) was proposed [15]. This method consists in the formation of analyte volatile compounds from the sample by the interaction between an organic precursor added to the sample and the ultraviolet light from the photochemical reactor. Then, the obtained volatile compounds are separated from the residual solution and carried to the detection system. In 2007, He et al. [19] published a critical evaluation of the applications of PVG in atomic spectrometry and discussion about the advances of the technique. The authors emphasized several advantages of the method such as no need of using relatively expensive and/or unstable reagents such as tetrahydroborate, that makes the method simpler, greener and in most cases cost-effective, besides the expanded number of detectable elements. Moreover, due to the higher tolerance to interferences, a drastic digestion of the sample is often unnecessary, as in the case of Hg determination in biological tissues solubilized with formic acid [20,21] or tetramethylammonium hydroxide [21]. Other examples are the direct determination of Hg in ethanol fuel [22] and wine and liquors [23].

In ten years of existence, several investigations have been done that help the understanding of the process occurring during photochemical vapor generation. However, there are still few applications to real samples. Based on the best of our knowledge, the use of PVG for determination of Hg in petroleum derivatives has not been published yet.

The present work proposes the use of the photochemical vapor generation coupled with atomic absorption spectrometry for the direct determination of Hg in naphtha and petroleum condensate samples. The objective is to obtain a simple, fast and accurate method using detergentless microemulsions as sample preparation, avoiding digestion procedures.

2. Experimental

2.1. Instrumentation

A photochemical reactor, consisting of spiral quartz tubing ($115 \text{ cm} \times 1.3 \text{ mm i.d} \times 3.0 \text{ mm o.d}$, Internal volume: 2.3 mL) wrapped around of a low-pressure Hg vapor UV lamp (254 nm, 18 W, TUV PL-L, Philips, Poland), was constructed.

Samples were propelled through the photochemical reactor with the assistance of a Reglo peristaltic pump (Ismatec, Switzerland). A flow of nitrogen (Air liquide, Canoas, Brazil) was introduced in the line after the photochemical reactor to carry the volatile species; the flow rate was controlled by a flow meter (Cole Parmer, Vernon Hills, IL, USA). The volatile species formed mixed with the nitrogen were introduced in a gas-liquid separator to separate the residual waste from the gaseous phase. After the separation, the volatile species were transported to a quartz tube ($10 \text{ mm i.d} \times 10 \text{ cm length}$) for atomic absorption measurements. Measurements were performed with an AAS 6 Vario Atomic absorption spectrometer (Analytik Jena, Jena, Germany) equipped with a deuterium background corrector. An Hg hollow cathode lamp (Narva G.L.E., Berlin, Germany) was used as line source, operating at 5 mA and slit of 1.2 nm, and the wavelength was set at 253.7 nm. Measurements were available in peak height mode. A schematic of the system is illustrated in Fig. 1.

2.2. Reagents and samples

Analytical grade reagents were used for all experiments. The inorganic working standards were daily prepared by dilution of the 1000 mg L^{-1} Hg stock solution (Mercury (II) nitrate, Merck, Darmstadt, Germany) with distilled, deionized water with a specific resistivity of $18 \text{ M}\Omega\cdot\text{cm}$ obtained from the Milli-Q water purification system (Millipore, Bedford, MA, USA). The organic working standards were prepared by dilution of the $100 \mu\text{g g}^{-1}$ Hg stock solution (Mercury Alkyl Dithiocarbamate, Conostan, Ponca City, OK, USA) with propan-1-ol (Merck). Formic acid 85% (v/v) (Synth, Diadema, SP, Brazil) was investigated as low molecular weight organic precursor (LMWOP) to obtain the photochemical vapor generation. Propan-1-ol and butan-1-ol (J.T. Baker, USA) were used in the microemulsion preparation. Naphtha and petroleum condensates were provided by Brazilian refineries.

2.3. Sample preparation

The sample preparation consisted in the formation of 2.0 mL of microemulsion. The adopted composition for the microemulsions was: sample (50% v/v), propan-1-ol (48% v/v) and water (2% v/v). In the microemulsions for calibration the inorganic or organic Hg standards ($0.0, 25.0, 50.0, 75.0$ and $100.0 \mu\text{g L}^{-1}$) were mixed just with propan-1-ol. Recovery tests with inorganic and organic Hg standards have been performed for one naphtha and two petroleum condensate samples. In the microemulsion preparation, the microemulsified samples were spiked with 100 and 200 ng of inorganic or organic standards. For all measurements the microemulsions were prepared in triplicate

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