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ISSN 0350-350X
GOMABN 52, 1, 35-40
Izvorni znanstveni rad / Original scientific paper

DETERMINATION OF LOW ARSENIC CONCENTRATIONS IN LIGHT GASOLINE BY GFAAS TECHNIQUE

Abstract

The main parts of the light naphtha isomerization unit in oil refinery are reactors loaded with platinum base catalyst. Even small amount of water, sulfur, oxygenates and/or nitrogen is poisonous for the catalyst. In addition, the catalyst activity is negatively affected by metals. Arsenic, one of the metal poisons, decreases the catalyst activity in µg/l quantity. Therefore, it's crucial to detect it precisely in order to protect the expensive platinum based catalyst in time.

A procedure for determination of arsenic in light gasoline at µg/l levels by graphite furnace atomic absorption spectrometry (GFAAS) is proposed. GFAAS is good alternative for the determination of trace metals in petroleum fractions and distillates to relatively expensive ICP-MS. Sample stabilization was achieved by mixing appropriate volumes of the sample, propan-1-ol and nitric acid aqueous solution. This mixture resulted in one-phase medium (microemulsion), which was indefinitely stable. $Pd(NO_3)_2$ *solution was used as modifier. Validation of the method includes microemulsion stability, linearity, yield, precision, limit of detection and limit of quantification.*

Keywords:
isomerization, platinum based catalyst, arsenic, gasoline, GFAAS, validation

Introduction

In March 2011 the final construction works were completed on the new light naphtha Isomerization unit in the INA d.d. Sisak Refinery, and the unit was started up in January 2012.The unit consists of the LNHT section (light naphtha hydrotreating) and the Penex section (light gasoline isomerization)[1]. The goal of the Penex section is to increase the octane number of the gasoline feed from 70 to 90 by isomerization of the linear C5/C6 hydrocarbons to their corresponding branched-chain isomers. In order to remove catalyst poisons such as metals (As, Hg, Pb, Ca, Na and Si), which permanently deactivate the catalyst; as well as sulfur, nitrogen and oxygenates, which are temporary poisons; the feed for Penex is hydrotreated in the LNHT. The product of gasoline isomerization is called isomerate and is a mixture of mostly high octane number components, 2,2-dimethylbuthane and 2,3-dimethylbuthane.

The Sisak Refinery Isomerization unit catalyst is one of the new types of catalyst for isomerization reactions in light gasoline stream. The catalyst is made of 2 components: the metal and the support. Platinum is employed as metal while highly active chlorinated aluminum oxide (Al_2O_3) serves as support. Acidity of the catalyst is increased by treating aluminum oxide with halogen component, i.e. by continuous injection of organic chlorides into the feed, which are converted to hydrogen chloride at reactor temperatures. Despite the continuous maintenance of catalyst activity by chlorides injection and process temperature adjustment, it is important to keep the catalyst highly active for isomerization reactions over a long period of time. Heavy metals, such as arsenic, are permanent poisons for platinum based catalysts.[2] Platinum atoms, which are active in the desired catalytic reactions, are involved in the chemisorption of the reactants (and of poisons as well) via their orbitals. Accordingly, any chemical species having a proper electronic configuration (e.g. unoccupied orbitals or unshared electron) or multiple bonds (e.g. CO, olefins, etc.) can be considered as potential poisons for the catalyst. Arsenic, in the form of arsine (AsH_3), having a lone electron pair, is a strong poison in hydrogenation reaction that take place on the metal component of the platinum base catalysts.[3] Arsenic is present in feed in small quantities and its influence on deactivation is noted after some time when the coke can be the reason for catalyst deactivation as well. As arsenic is the permanent catalyst poison which cannot be removed; the catalyst loses its desired activity and has to be replaced with the fresh one. The financial consequences of that replacement are very negative. Therefore, it is crucial to detect arsenic precisely in feed in order to protect the expensive platinum base catalyst in time.

Graphite furnace atomic absorption spectrometry (GFAAS) has been successfully used for analysis of petroleum products due to its high sensitivity (limits of detection in the range from $\mu g\ L^{-1}$ to $ng\ L^{-1}$)[4]. GFAAS offers high selectivity, simplicity, work with complex matrices and relatively low costs of equipment for routine analysis. Direct analytical techniques are preferred for routine analysis over those that require significant sample preparation. The direct introduction of fuel samples for metal determination presents some general problems, such as volatility, flammability and immiscibility with water, difficulty of sample introduction due to low viscosity and surface tension, excessive spreading of the fuel during thermal pretreatment in GFAAS due to the temperature gradient (when longitudinally heated atomizers are used). When samples are prepared by dilution with organic solvents, changes in analyte concentration within a short period of time are often observed, due to solvent volatilization and/or sorption of the trace metals on the walls of containers. The use of emulsions and microemulsions appears to be most efficient because they dont't require long preparation time and also decrease the risk of losses caused by volatilization or sorption[5,6].

Experimental

Instrumentation, materials and reagents

Measurements were performed with a model Zeenit 650 (Analytik Jena) atomic absorption spectrometer, equipped with Zeeman background correction. An As hollow cathode lamp operated at current of 10 mA was used as line source. The measurements were performed at 193.7 nm, with the slit fixed at 0.8 nm. Argon with a purity of 99.999 % (Messer) was used with a flow rate of 2 L min^{-1} during all stages, except during atomization, when the flow was stopped.

Only high purity reagents were used. Commercial chemicals were used without further purification. Ultra pure water with conductivity of 0.055 μS cm^{-2} from purification system (TKA Smart2Pure System) was used for preparation of standards, microemulsions and modifier solutions. All glassware was immersed in 5 % HNO_3 for at least 24 h, rinsed with ultra pure water and dried before use. Only A class volumetric glassware was used. The working standards were prepared by dilution of 1000 mg L^{-1} As stock solution (Fluka, $NaAsO_2$) with 0.5 % $HNO_{3.}$ $Pd(NO_3)_2$ (Merck, deluted with 0.5 % HNO_3 to obtain 2 g L^{-1} solution) was used as the modifier. Samples (feed for Isomerization unit, light straight run gasoline or light gasoline) were colected at Sisak refinery and stabilized immediately after sampling.

Stabilization of the samples

Samples were stabilized immediately after sampling by mixing 3 mL of sample with 6.4 mL of propan-1-ol and 600 µL of nitric acid solution (0.014 mol L^{-1}). The mixture was shaken in order to obtain a transparent solution (microemulsion).

Procedure for arsenic determination

Inorganic As standard was used for calibration (10 µg L^{-1} As standard was prepared and further dilutions were carried out by instrument). According to literature data[5], it is necessary to introduce at least 30 µL of stabilized sample (microemulsion) in order to improve sensitivity. Since the maximum volume that could be injected into atomizer was 40 µL, three aliquots of 30 µL of microemulsion were introduced into the graphite tube, and each injection was followed by 5 µL of modifier solution.

Table 1 showes temparature program used for arsenic determination in light straight run gasoline samples.

Table 1: Temperature program for arsenic determination in light straight run gasoline samples, stabilized as microemulsion.

Step	**Temperature / °C**	**Ramp / °C s^{-1}**	**Hold / s**
Drying	75	1	5
Drying	150	2	3
Pyrolysis	947	100	25
Auto-zero	947	0	5
Atomization	2400	1000	3
Cleaning	2650	1000	3

Results and discussion

Stability of solutions

Method proposed by Becker et al. (sample stabilization as microemulsion)[5] provided clear, transparent solution. Because of minimal sample preparation, the risk of sample loss and sample contamination is decreased. These problems are related to diverse sample pretreatments such as extraction, combustion and chemical mineralisation. Moreover, dilution factors are small, avoiding prohibitive decrease of the limit of detection. Stability of microemulsion was observed during 3 days. Fig. 1 shows concentration of As in a light gasoline sample prepared as a microemulsion with 16 µg L^{-1} As inorganic standard during 48 h. Microemulsion was stable during 48 h, a period which is sufficient for routine analysis.

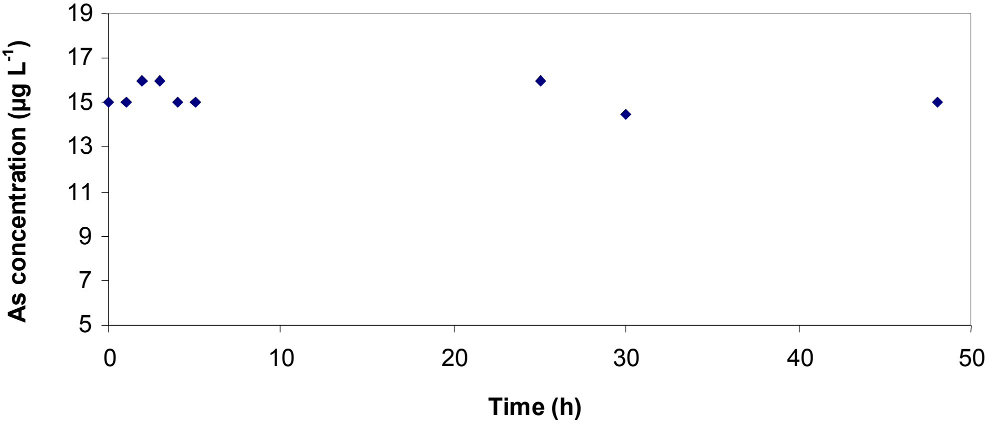

Figure 1: Stability of the microemulsion: concetration of As in microemulsion with inorganic As standard (16 µg L^{-1}) during 48 hours.

Temperature parameters

In first stage (drying) slow heating ramp was used to prevent loss of sample due to spattering and ensure adequate removal of volatile components of the matrix. Three aliquats of 35 µL of sample were introduced, each one followed by injection of 5 µL of modifier solution. Due to high volatility of As, temperature of the pyrolysis should be as low as possible to prevent analyte losses but high enough to complete matrix removal. As described in literature, measurement of an analytical signal for As in gasoline samples was only possible using pyrolysis temperatures higher then 900 °C due to the high background absoption caused by the vaporisation of the matrix when lower pyrolysis temperatures were used. After optimizing conditions, pyrolysis temperature of 947 °C and an atomization temperature of 2400 °C have been choosen for further deteminations (Table 1).

Arsenic is known to be volatile element and losses might occur even at low pyrolysis temperatures (200 °C – 400 °C) when no chemical modifier is used, which means that the use of chemical modifier in As determination in petroleum products is absolutely neccesary. Due to the fact that paladium is the most used modifier for As determination in organic matrixes[6,7], $Pd(NO_3)_2$ has been used in this research.

Method validation and determination of arsenic in light straight run gasoline sample

Aqueous As standard solution was used for calibration. Linearity was tested up to 20 μg L^{-1} (region of interest). Obtained coefficient corelation, *r*, is 0.9995. Limits of detection (LOD) and quantification (LOQ) were calculated from 10 measurements of the analytical blanck (6.4 mL of propan-1-ol + 600 μL of 0.5 % HNO_3) and are defined as arsenic concetration that gives a response equivalent to three and ten times, respectively, of the standard deviation of blanck average values. Values obtained were 1.5 μg L^{-1} and 5.0 μg L^{-1}. LOD and LOQ were also determined experimentaly, values obtained were 1 μg L^{-1} and 5.0 μg L^{-1}.

Arsenic wasn't detected in the analysed light straight run gasoline sample, which means that As was not present in the sample or his concetration was below LOD.

Due to the fact that As wasn't detected in the sample, the precision (repeatability) was calculated from 10 consecutive measurements of stabilised sample spiked with inorganic As standard (10 μg L^{-1}). The precision of the method is difined as the relative standard deviation (RSD). Obtained value is 9.0%. Due to the lack of certified reference materials, the accuracy was checked using recovery experiments. The sample was spiked with 16 μg L^{-1} As standard solution (n = 5), recovery result was 94%.

Conclusion

The determination of As in petroleum products by GFAAC using microemulsion can be considered an interesting alternative for routine analysis. The main goal of this work, the development of rapid and reliable method to determine arsenic in light straight run gasoline, could be realized by preparing a microemulsion of a sample and calibration using inorganic standard in aqueous solution. This procedure allows determination with minimum of sample pretreatment and stabilization of analyte for sufficiently long period between sample preparation and the analysis minimizing errors due to analyte losses. The use of chemical modificator was mandatory for stabilization of analyte. The use of inorganic standards in aqueous solution for calibration greatly reduces the cost and analysis time.

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Received
2.10.2012.

Accepted
27.11.2012.