



Aromatic amines quantification in gasolines by GC-VUV

Vehicle efficiency is a key driver to significantly contribute to reducing greenhouse gas (GHG) emissions and accelerating the decarbonisation of the road transport sector. This improvement can be sought in better engine mechanical efficiency as well with a high performance fuel. Concawe, the European association of refiners which carries out research in the field of petroleum products, has conducted a theoretical study on the impact of CO₂ emissions and the technical feasibility of the production of high octane petrol (HOP) with promising results (1). This study showed that using HOP gasoline can increase engine efficiency by up to 1% for each Research Octane Number (RON) increase point compared to standard 95 and 98 octane gasoline. This results in a reduction of CO₂ emissions.

A particular class of compounds, among the octane boosters that can be present in HOP gasolines, are aromatic amines, in particular the molecules:

- aniline (CAS 62-53-3)
- N-methylaniline (CAS 100-61-8)
- N,N-dimethylaniline (CAS 121-69-7)
- N-ethylaniline (CAS 103-69-5).

Nowadays this class of compounds can be added to petrol and there is no specific limit.

The aim of this work was to set up a GC-VUV method to quantify aromatic amines in automotive gasoline together with the analysis for DHA compounds (detailed hydrocarbon analysis) and PIONA classes (paraffins, isoparaffins, olefins, naphthenes and aromatics). The data obtained were compared with values of total nitrogen obtained in chemiluminescence.



Agilent 8890 GC - VGA-100 VUV ANALYTICS

VUV - Vacuum ultra violet detector:

In the spectral region between 120 and 240 nm, many organic compounds show strong absorption due to forbidden electronic transitions at higher wavelengths, typical areas of the near ultraviolet and the visible regions. The Vacuum Ultraviolet (VUV) photons have energy such as to induce electronic transitions in virtually all molecules involving the $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ states, thus making even simple alkanes analysable. The possibility of recording a spectrum attributable to these molecular electronic transitions therefore allows us to unambiguously recognize molecules and classes (e.g. DHA, PIONA). The VGA-100 GC detector operates in the Vacuum Ultraviolet (VUV) zone and allows to perform both qualitative and quantitative analyses. Absorption spectra are specific for each compound and provide unprecedented selectivity to uniquely identify compounds in complex mixtures, including coeluting isomers (VUV patent).

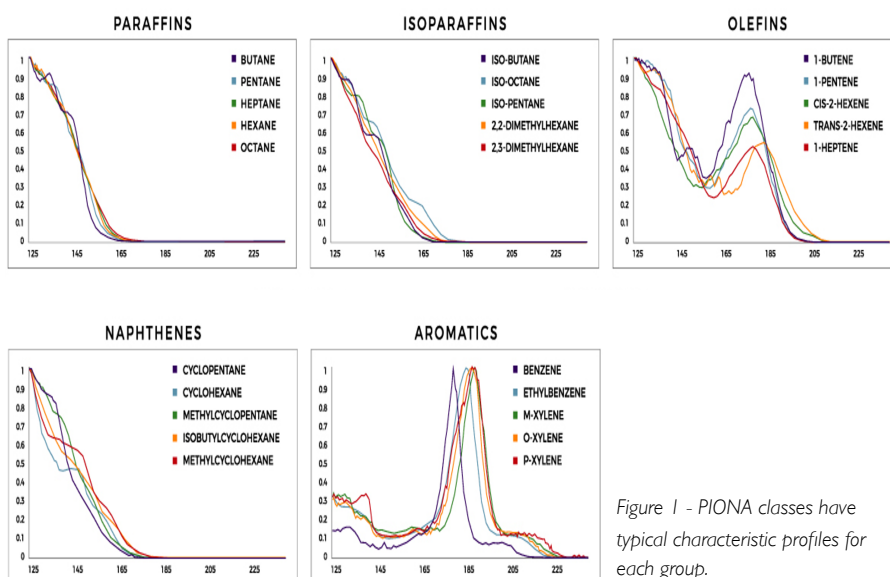


Figure 1 - PIONA classes have typical characteristic profiles for each group.

Setting up the method:

The VGA-100VUV detector is supplied with a DHA (Detailed Hydrocarbon Analysis) method to determine the main molecules listed by the ASTM 6730 method; however, this method does not provide the speciation of any aromatic amine. The method was therefore modified in order to have a better chromatographic separation on the molecules of interest and perform quantification measurements.

Adding spectra to VUV library and calculating response factors:

Reference mixtures were prepared by weighing molecules of interest in dichloromethane in order to add a reference spectra to the library. A known quantity of toluene was added together with the nitrogenous compound in order to calculate the response factor according to the formula:

$$\frac{RRF_2}{RRF_1} = \frac{M_2}{M_1} \frac{A_1}{A_2}$$

Where M_2 / M_1 is the relative mass of the two and A_1 / A_2 is the ratio of the measured areas.

After that, the retention index according to Kovats was calculated with the formula:

$$RI_i = 100 * \left[n + \frac{t_i - t_n}{t_{n+1} - t_n} \right]$$

Spectrums of pure compounds are clearly distinguishable from each other and describe the molecular electronic transitions typical of each structure.

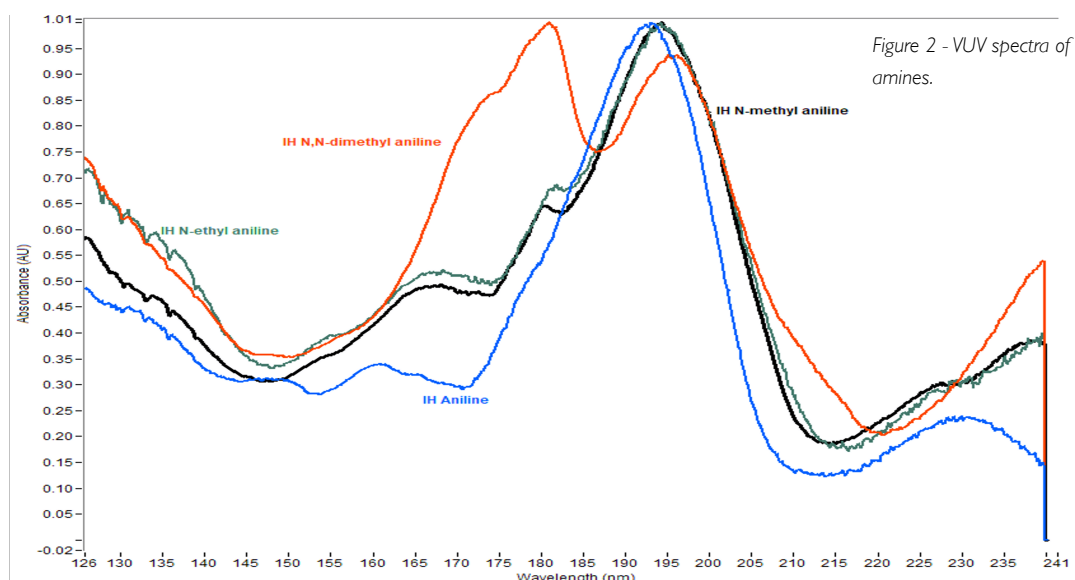


Figure 2 - VUV spectra of aromatic amines.

It can be seen that the peak at 195 nm is typical of aromatic rings structures and moves to higher λ wavelengths as the number of alkyl substituents bonded to the nitrogen increases. This is because the substituent groups $-NHCH_3$, $-N(CH_3)_2$ and $-NHCH_2CH_3$ act as strong ring activators ("electron pumps") facilitating the resonance of the aromatic system and therefore the electronic transition. Consequently, a smoother electronic transition is synonymous with absorptions at higher λ because, according to Plank's law:

$$E = \frac{c}{\lambda}$$

Where E is the energy associated with the photon and λ the wavelength. An inversely proportional relationship between E and λ then follows.

Where t_n and t_{n+1} s are the retention times of the following and previous alkane and n is the number of carbon atoms of the alkane preceding the peak of interest.

Here are the values obtained:

		CAS	RRF	RI (Kovats non polar)
Aniline		62-53-3	0,211	950
N-methylaniline		100-61-8	0,236	1038
N-ethylaniline		121-69-7	0,256	1069
N,N-dimethylaniline		103-69-5	0,243	1104

The response factors obtained are all around same values and it is not surprising as the molecular structure of the amines in question is very similar and therefore also their molar extinction coefficient.

Results:

First, the quantification of an aromatic amine, taken as a reference (N-methylaniline) in standard samples constructed by weighing starting from gasolines, was evaluated. The quantification turns out to be accurate as can be seen from the calibration curve obtained:

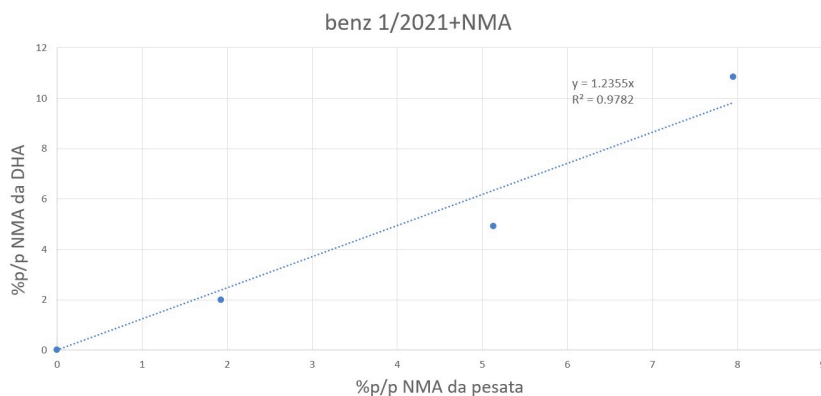
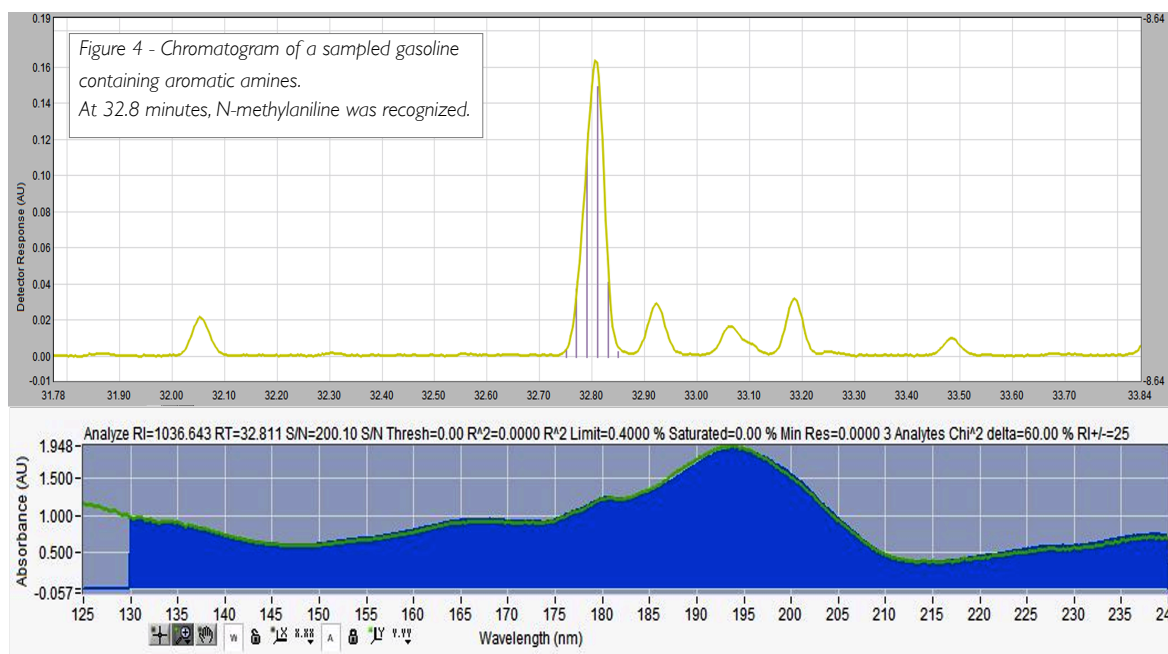


Figure 3 - Calibration line obtained from three spikes in a gasoline free from aromatic amines.

At this point, real samples were analysed. Below the chromatogram of a gasoline containing N-methylaniline (Fig. 4).



As can be seen in Fig. 5, the software automatically recognized a coelution between N-methylaniline and 1,3-Diethylbenzene by correctly assigning the mass contribution to both analytes. This is because the spectra of the two molecules are different, and both contribute to forming the total UV spectrum.

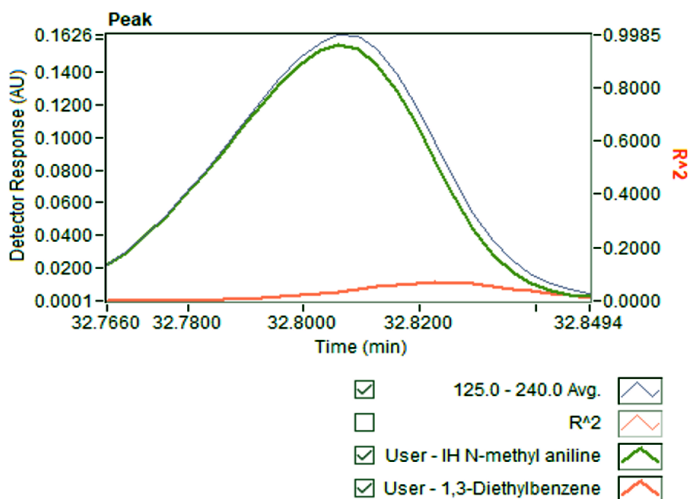


Figure 5 - Coelution between NMA and 1,3-Diethylbenzene. In blue the total chromatographic peak and in red/green the assignment made automatically by the software which deconvolves the coelution of the two compounds.

	N-methylaniline	1,3-Diethylbenzene
Allocated area	94.3%	5.7%

Comparison with analyses carried out in chemiluminescence (total nitrogen data):

	NMA (mg/mL)	N from NMA (mg/kg)	N (mg/kg) obtained in chemiluminescence
Gasoline A	27.11	4529	4943
Gasoline B	25.49	4361	4734

From the comparison between the two techniques it can be noticed that VUV data are very close to those obtained with the elemental analysis in chemiluminescence which determines nitrogen as a total. The underestimation of the VUV may be due to the fact that some nitrogenous compounds present in petrol may not be aromatic amines but other nitrogenous compounds, probably inorganic.

Conclusions:

Using GC-VUV was possible to implement an existing DHA method by adding extra compounds. This advantage is characteristic of a versatile technique such as the VUV one and can also be extended to other compounds of interest.

Thanks:

A special thanks goes to Dr. Martina Martini and Dr. Simone Lixi of Innovhub, San Donato Milanese - Italy.

Note:

(1) Valdenaire, D.; Hamje, H. High-Octane Petrol (HOP) Study: Making Gasoline Relevant for the Future of Road Transport; Concawe: Brussels, 2019. www.concawe.eu/wp-content/uploads/HOP-28.1.pdf

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