

# Arsenic determination in naphtha by electrothermal atomic absorption spectrometry after preconcentration using multiple injections

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Naphtha is a petroleum fraction containing C4–C15 hydrocarbon compounds and is used as feedstock for petrochemical processes which are affected profoundly by trace amounts of arsenic. A simple method for arsenic determination in naphtha using electrothermal atomic absorption spectrometry with polarized Zeeman-effect background correction was developed. Multiple injections were used for direct preconcentration in the graphite tube, eliminating sample pretreatment. Doehlert experimental designs were used to find the best settings for the furnace program parameters. Modifier concentration, number of multiple injections and sample volume were also optimized with the same multivariate approach. With three 45  $\mu\text{L}$  sample injections, ashing temperature 1200  $^{\circ}\text{C}$ , atomization temperature 2700  $^{\circ}\text{C}$  and ashing time 60 s, a detection limit of 0.5  $\mu\text{g L}^{-1}$  and a characteristic mass of 61 pg were achieved, using 3000  $\text{mg L}^{-1}$   $\text{Pd}(\text{NO}_3)_2$  as the chemical modifier. The relative signal standard deviation was found to be 9.0% at the 2.3  $\mu\text{g L}^{-1}$  level. Results from several naphtha test samples showed arsenic levels typically below 3.0  $\mu\text{g L}^{-1}$ . The high degree of automation of the proposed method minimized technician sample handling allowing its application for routine analysis. This procedure has been used for arsenic determination in naphtha feeds processed in the Braskem Petrochemical (Salvador, Bahia, Brazil).

## Introduction

Naphtha is a petroleum fraction comprised of a complex mixture of more than a hundred C4–C15 hydrocarbon compounds. It is the main stream used by petrochemical industries for producing a wide range of chemical products such as benzene, toluene, xylenes, ethylene, propylene, *etc.*

Determination of arsenic is important for various cracking processes in petrochemical plants because even trace concentrations can cause severe and irreversible catalyst poisoning during naphtha cracking.<sup>1–4</sup> Although arsenic tends to concentrate in the heavier fractions of petroleum,<sup>1,5</sup> it is essential to monitor the low levels of this contaminant in naphtha because thousands of tons per day are processed and this element shows the tendency for accumulating in the catalyst beds. Besides, release of toxic elements into the environment should, of course, be avoided. Typical arsenic concentration in naphtha ranges from <1 to 40  $\mu\text{g L}^{-1}$ .<sup>2,6–13</sup>

In 1959, Powers *et al.* suggested arsenic would be present in naphtha as alkyl arsines.<sup>2</sup> Studies conducted by Puri and Irgolic in 1989 revealed that trimethylated and monomethylated arsenic are, in fact, the predominant arsenic species in petroleum products.<sup>14</sup>

The main features of some literature reports on analytical methods for arsenic determination in naphtha samples are summarized in Table 1. Some papers published by the end of the 50's proposed different approaches for quantifying arsenic in naphtha. In 1957, Maranowski *et al.* developed a reflectometric method in which arsenic was isolated on a piece of paper as the colored reaction product between arsine and mercuric bromide after wet oxidation.<sup>7</sup> In the following years, other

authors proposed different methodologies based on spectrophotometric determinations of arsenic as molybdenum blue or silver diethyldithiocarbamate complexes.<sup>2,6,8,9</sup> Those methods all have in common the laborious and time-consuming sample pretreatment step for matrix separation or analyte preconcentration, such as wet acid digestion, combustion, liquid–liquid extraction, distillation and arsine generation.

In 1981, Shaw *et al.* proposed a method using neutron activation analysis (NAA) for several oil products, including naphtha.<sup>5</sup> The method required minimal sample preparation and was applied to several elements besides arsenic. Although the limit of detection is not clearly stated, the minimum arsenic concentration found in a wax sample was 0.07 ppm. Arsenic determination in naphtha was also tried using inductively coupled plasma atomic emission spectrometry (ICP-AES).<sup>10</sup> Using such a technique, Botto *et al.* observed a severe matrix interference attributed to aromatics absorption in the UV wavelength used for analysis. As a consequence, quite high limit of detection (20  $\mu\text{g L}^{-1}$ ) and unacceptable relative standard deviation (60%) at this concentration level were observed. More recently, arsenic determination in naphtha samples has been performed using methods based on inductively coupled mass spectrometry (ICP-MS).<sup>11–13</sup> Olsen *et al.* proposed a method using a conventional Meinhardt–Scott chamber, achieving a limit of detection of 0.2  $\mu\text{g kg}^{-1}$  with sample dilution in xylene (1 + 6.5 m/m).<sup>11</sup> Botto used xylene for dilution of naphtha but also suggested the use of other solvents such as a mixture of hexane and 2-propanol in order to minimize the formation of deposits around the direct injection nebulizer (DIN) capillary.<sup>12</sup> With this method the limit of detection ranged from 0.04 to 0.2  $\mu\text{g kg}^{-1}$ , depending

**Table 1** Summary of literature references on arsenic analysis in naphtha samples

Ref.	Sample pretreatment	Analysis technique	Limit of detection	As found in samples
2	Solid phase extraction onto silica gel + wet acid digestion + arsine generation	Spectrophotometry (silver dithiocarbamate reagent)	not stated	4.0–9.2 ppb
6	Combustion in an oxyhydrogen burner + absorption in a NaOH solution + arsine generation	Spectrophotometry (silver dithiocarbamate reagent)	2 ppb	2–8 ppb
7	Wet oxidation + arsine generation + isolation of arsenic on paper	Diffuse reflectance spectrophotometry (mercuric bromide reagent)	2 ppb	15–25 ppb
8	Wet oxidation + liquid–liquid extraction + distillation	Spectrophotometry (as the arsenic-molybdenum blue complex)	1 ppb	4–51 ppb
9	Wet oxidation + liquid–liquid extraction + arsine generation	Spectrophotometry (silver dithiocarbamate reagent)	0.4ppb	13–89 ppb
5	None	Neutron Activation Analysis	< 1 ppm	not detected
10	None	ICP-AES	20 $\mu\text{g L}^{-1}$	not stated
11	Sample dilution	ICP-MS	0.2 $\mu\text{g kg}^{-1}$	not stated
12	Sample dilution	ICP-MS	0.04–0.2 $\mu\text{g kg}^{-1}$	< 1–67 $\mu\text{g kg}^{-1}$
13	Sample emulsification	ICP-MS	0.1 $\mu\text{g L}^{-1}$	0.64–0.9 $\mu\text{g L}^{-1}$
This work	None	ETAAS	0.49 $\mu\text{g L}^{-1}$	0.59–2.89 $\mu\text{g L}^{-1}$

on the solvent used for sample dilution (1 + 4 m/m). Kumar *et al.* used a Triton X-100 aqueous solution instead of xylene or tetralin for naphtha dilution (2 + 1 v/v) in ICP-MS analysis.<sup>13</sup> The oxygen present in the water-in-oil emulsion helped to prevent carbon buildup on the plasma cones, dispensing the use of additional organic diluents. A somewhat lower limit of detection (0.1  $\mu\text{g L}^{-1}$ ) was thus obtained, compared to the previous works. It is worth noting that problems such as carbon deposition and alteration of plasma properties have to be faced when organic matrices are analysed by ICP-MS.

In the present work we report on the use of multiple injections for direct arsenic preconcentration in naphtha for electrothermal atomic absorption spectrometry (ETAAS) analysis. ETTAS has been successfully used with many complex matrices and presents the advantage of being a less expensive technique compared to ICP-MS and thus more accessible to most industry laboratories. Some procedures have been developed for several matrices, with detection limits in the 5–10  $\mu\text{g L}^{-1}$  range with single injection. These procedures, however, are not sensitive enough for most naphtha samples and usually include time-consuming preconcentration steps and analyte addition technique for calibration. From an industrial point of view, this could lead to unacceptable delays in releasing the analytical result and thus preclude their use in routine analysis. Multiple injections could speed up the analysis by dispensing sample pretreatment steps and help overcome the delaying problem.

Multiple injection technique has been applied to *in situ* preconcentration of several metals such as nickel,<sup>15,16</sup> manganese,<sup>16</sup> cobalt,<sup>16</sup> iron,<sup>16</sup> copper,<sup>16,17</sup> molybdenum,<sup>18,19</sup> cadmium,<sup>20,21</sup> lead,<sup>22</sup> silicon<sup>23</sup> and chromium.<sup>16,24</sup> With this procedure, limits of detection in the ng  $\text{L}^{-1}$  level have been reached. No literature reference appears to be available on using multiple injections or ETAAS for arsenic analysis in naphtha samples. Furthermore, volatility of arsenic species is a matter of concern and special care has to be taken to avoid loss of such volatile species through the successive drying steps.

The methodology proposed in this work was subjected to a multivariate optimization study based on Doehlert designs,<sup>25</sup> which use a minimum number of experiments for assessing the influence of each experimental setting on the desired analytical responses and identifying possible interactions between them. Optimum conditions can be sought by locating the mathematical extrema of functions fitted to the responses obtained from the experimental runs based on the Doehlert design. The literature on using multivariate optimization techniques in ETAAS appears to be quite limited, as yet.<sup>26–29</sup>

## Material and methods

### Apparatus

All experiments were carried out in a Zeeman electrothermal atomic absorption spectrometer (Varian, model Spectra AA220Z) equipped with an autosampler (Varian, model PSD 100) and connected to a Dell PC. The spectrometer's graphite tubes were designed with an integrated platform attached to a single point, providing minimal contact with the tube and more uniform heating. Argon 99.998% (White Martins, Brazil) was used as the purge gas. The hollow cathode lamp (arsenic UltraAA lamp, Varian) was operated at 193.7 nm with 10 mA current and 0.5 nm spectral bandwidth.

### Reagents and solutions

All reagents used were of standard analytical grade. Deionised water was obtained from a Mili-Q Reagent-grade Water System (Milipore, USA), resistivity 18  $\text{M}\Omega \text{cm}^{-1}$ .

An arsenic standard stock solution of 100  $\text{mg kg}^{-1}$  was supplied by Conostan (Conostan Oil Analysis Standards, Ponca City, OK, USA). The arsenic solution was available in a base oil with a specific gravity of *ca.* 0.85. All working standard solutions were prepared from the stock solution on a daily basis, using the Braskem internal product known as mixed xylenes (MX) as solvent. The typical MX composition is 50% m/m ethyl benzene, 25% m/m *m*-xylene, 13% m/m *p*-xylene, 8% m/m *o*-xylene and 4% m/m other aromatic compounds.

Palladium modifier solutions (417, 2000, 3000 and 3582  $\text{mg L}^{-1}$ ) were prepared in 0.1% v/v  $\text{HNO}_3$  from a stock solution of 10000  $\text{mg L}^{-1}$   $\text{Pd}(\text{NO}_3)_2$  in *ca.* 15% v/v  $\text{HNO}_3$  (Merck, Darmstadt, Germany).

Nitric acid 60% v/v was of Ultrapur grade, supplied by Merck (Darmstadt, Germany).

### Samples

All naphtha samples were collected into clean bottles and stored in a freezer at 4 °C prior to analysis, usually performed within three days. The sampling apparatus was cleaned by nitric acid, deionised water and ethanol washings. The samples were collected from the plant's raw material storage tank or directly from carrier ship tanks. Typically, the naphtha samples presented distillation curves ranging from 30 to 280 °C and specific gravity values around 0.70.

**Table 2** Graphite furnace temperature program

Cycle	Step	Temperature/°C	Time/s	Argon flow/L min <sup>-1</sup>	Read	Signal storage
Drying	1	90	2.0	3.0	No	No
	2	115	15.0	3.0	No	No
	3	120	10.0	3.0	No	No
	4	90	1.5	3.0	No	No
	5	180	15.0	3.0	No	No
Ashing	6	1200	10.0	3.0	No	No
	7	1200	60.0	3.0	No	No
	8	1200	2.0	0	No	Yes
Atomization	9	2700	0.8	0	Yes	Yes
	10	2700	2.0	0	Yes	Yes
	11	2700	0.8	3.0	No	Yes
Cleaning/cooling	12	90	18.0	3.0	No	No

### General analytical procedure

The naphtha sample is slowly injected at a rate of *ca.* 2.5  $\mu\text{L s}^{-1}$  into the graphite tube preheated at 90 °C, where preconcentration takes place. Three successive 45  $\mu\text{L}$  sample aliquots are delivered to the tube and the temperature is raised, leading to partial drying of each aliquot. A 6  $\mu\text{L}$  aliquot of the 3000  $\text{mg L}^{-1}$  Pd modifier solution is co-injected with each sample aliquot. At each multiple injection, the sample and modifier aliquots are dried through steps 1–4 described in Table 2, before the next injection. After the third injection, the temperature program is completed according to the conditions shown in the table and the total amount of arsenic is determined from the integrated absorbance signal. All these settings were used for sample analysis, and some were varied in the optimization experiments described below. Following the stabilized-temperature platform furnace (STPF) concept,<sup>30</sup> signals were recorded as integrated absorbances, because calculations using peak heights exhibited worse data precision, in spite of a slightly better sensitivity.

### Optimization strategy

In a Doehlert design, the experimental points are uniformly distributed as a rhombic lattice in the variable (factor) space. For two factors, this would be a hexagon. For  $k$  factors, the design requires ( $k^2 + k + 1$ ) experiments, in which at least three levels are assigned to each factor. Our research group has used Doehlert matrix for optimization of several preconcentration procedures for metal determination by ICP OES<sup>31</sup> and FAAS.<sup>32</sup> The optimization study was carried out in two steps, based on different Doehlert designs. First, all important furnace program variables were investigated, together with the modifier concentration. The selected program variables were ashing hold time ( $t_{\text{ash}}$ ), ashing temperature ( $T_{\text{ash}}$ ) and atomization temperature ( $T_{\text{at}}$ ). The modifier concentration,  $[M]$ , was also included, because a relation between this factor and ashing/atomization variables was expected.

In a subsequent step, the variables related to the total sample volume, sample aliquot of each injection ( $V_s$ ) and number of multiple injections ( $N$ ), were investigated. All calculations were carried out using the *Statistica* software package.<sup>33</sup> The operational conditions of the drying steps were not included in the optimization, because the main response, sample sputtering, is qualitative.

The overall optimization process took into account the influence of the factor settings on three analytical responses: analyte signal, background signal and data precision. For the first design, the analytical responses were analyte signal ( $A_s$ ) and analyte to background signal ratio ( $R_{a/b}$ ). Precision was not evaluated at this stage, as a minimum of three replicates per experiment would be needed to ensure statistical significance. An ETAAS experiment consisting of so many runs could result in effect confounding due to tube aging.

For the second design, the response was followed in terms of analyte signal ( $A_s$ ), analyte to background signal ratio ( $R_{a/b}$ ) and signal relative standard deviation (RSD). The analyte and background signals were divided by a volume correction factor ( $f_v$ ), to eliminate the influence of different sampling volumes on the signals. The values presented in the tables below are therefore signals per unit volume. The volume correction factor was obtained as the product of the total volume of each aliquot by the number of multiple injections. The modifier volume was adjusted to keep a similar ratio to the sample volume at each experiment.

In the first, four-variable design, 21 experiments were carried out in duplicate and in random order, according to the specifications given in Table 3. The central point experiment (coded levels 0, 0, 0, 0) was repeated every fifth run, to confirm signal stability and allow for data correction due to tube aging, if needed. Some other experiments were repeated to check previous results. Ashing and atomization temperatures were investigated at 7 levels: ashing temperature ranged from 600 to 1900 °C and atomization temperature from 2364 to 2936 °C. Ashing time was studied at 5 levels (5 to 85 s), while modifier concentration was assessed at 3 levels (417, 2000 and 3582  $\text{mg L}^{-1}$ ). A 10.0  $\mu\text{g L}^{-1}$  arsenic standard in the MX solvent was used in this design. Three multiple injections of 35  $\mu\text{L}$  sample volume and 5  $\mu\text{L}$  modifier volume were used in all experiments.

In the second, two-variable design, 7 experiments were run in triplicate and in random order, according to the settings given in Table 4. The central point was repeated three times, to obtain a variance estimate. An eighth run was included as an additional point in the experiment and is not part of the original Doehlert design. The number of injections was varied in only three levels (1, 2 and 3), because more than 3 multiple injections could lead to undesirably large analysis times and background signals. Sample volumes were varied in 5 levels (15 to 55  $\mu\text{L}$ ). A 5.0  $\mu\text{g L}^{-1}$  arsenic standard in the MX solvent and the best experimental settings indicated by the analysis of the first design were used throughout.

### Method validation

The method was statistically validated at the best settings found in the optimization study. Precision was assessed with a spiked naphtha sample in which the final arsenic concentration was approximately 2.3  $\mu\text{g L}^{-1}$ . This solution was analyzed five times in four replicates, and the results were submitted to Cochran's test and ANOVA for assessing the homogeneity of the results obtained from the five data groups. Once data homogeneity was verified, the signal RSD was calculated and compared to the maximum acceptable RSD as given by the Horwitz criterion at that concentration level.<sup>34</sup> Accuracy was evaluated by analyte recovery from real naphtha samples spiked with 0.85, 1.36, 1.70 and 3.41  $\mu\text{g L}^{-1}$  arsenic. Sample spiking was used for accuracy assessment since a standard

**Table 3** Doehlert experimental design for the first optimization step. The factors are ashing hold time ( $t_{\text{ash}}$ ), ashing temperature ( $T_{\text{ash}}$ ), atomization temperature ( $T_{\text{at}}$ ) and modifier concentration [M]. The analyte signal and the analyte/background signal ratio are the responses. The experiments were run in duplicate and in random order. Values in parentheses are dimensionless coded factor levels

Run	$t_{\text{ash}}$ (s)	$T_{\text{ash}}/^{\circ}\text{C}$	$T_{\text{at}}/^{\circ}\text{C}$	[M]/mg L <sup>-1</sup>	Analyte signal (area)		Average signal ratio
17	85 (1)	1250 (0)	2650 (0)	2000 (0)	0.1669	0.1526	0.62
4	5 (-1)	1250 (0)	2650 (0)	2000 (0)	0.1888	0.1681	0.23
18	65 (0.5)	1900 (0.866)	2650 (0)	2000 (0)	0.0135	0.0152	1.44
22	25 (-0.5)	600 (-0.866)	2650 (0)	2000 (0)	0.1922	0.1693	0.14
25	65 (0.5)	600 (-0.866)	2650 (0)	2000 (0)	0.1921	0.1698	0.19
19	25 (-0.5)	1900 (0.866)	2650 (0)	2000 (0)	0.0102	0.0218	0.50
2	65 (0.5)	1467 (0.289)	2936 (0.816)	2000 (0)	0.1542	0.1329	0.82
					0.1343	0.1126	
9	25 (-0.5)	1033 (-0.289)	2364 (-0.816)	2000 (0)	0.1661	0.1609	0.26
20	65 (0.5)	1033 (-0.289)	2364 (-0.816)	2000 (0)	0.1853	0.1424	0.44
23	45 (0)	1683 (0.577)	2364 (-0.816)	2000 (0)	0.0935	0.1228	3.39
10	25 (-0.5)	1467 (0.289)	2936 (0.816)	2000 (0)	0.1837	0.1415	0.54
					0.1513	0.1372	
15	45 (0)	817 (-0.577)	2936 (0.816)	2000 (0)	0.1692	0.1580	0.23
13	65 (0.5)	1467 (0.289)	2721 (0.204)	3582 (0.791)	0.1772	0.1588	0.87
24	25 (-0.5)	1033 (-0.289)	2507 (-0.204)	417 (-0.791)	0.1763	0.1646	0.33
7	65 (0.5)	1033 (-0.289)	2507 (-0.204)	417 (-0.791)	0.1776	0.1636	0.42
					0.1497	0.1336	
12	45 (0)	1683 (0.577)	2507 (-0.204)	417 (-0.791)	0.1038	0.0657	1.53
5	45 (0)	1250 (0)	2864 (0.612)	417 (-0.791)	0.1274	0.1361	0.39
14	25 (-0.5)	1467 (0.289)	2721 (0.204)	3582 (0.791)	0.1863	0.1669	0.71
3	45 (0)	817 (-0.577)	2721 (0.204)	3582 (0.791)	0.2294	0.1924	0.26
8	45 (0)	1250 (0)	2436 (-0.612)	3582 (0.791)	0.2031	0.1938	0.54
1	45 (0)	1250 (0)	2650 (0)	2000 (0)	0.1715	0.1684	0.58
6					0.1438	0.1323	0.39
11					0.1920	0.1655	0.60
16					0.1857	0.1574	0.49
21					0.1789	0.1374	0.45
26					0.1676	0.1529	0.57

reference material is not available neither in naphtha nor in a suitable matrix such as xylene, toluene, light oils, *etc.* Additionally, there is no standard method (*e.g.*, ASTM) for arsenic determination in naphtha which could be used as a comparative method. The working linear range was defined by a minimum correlation coefficient of 0.998. The limit of detection was calculated from 10 replicates of a blank solution ( $3s_{\text{blank}}$  criterion). The sensitivity, or characteristic concentration, was obtained from the analytical curve as the concentration corresponding to an integrated absorbance of 0.0044 *s* and the characteristic mass was the equivalent mass calculated from the sensitivity value. Matrix interference was also investigated by comparing the slopes of the analytical curve and the analyte addition curves.

## Results and discussion

### Optimization of the drying steps

Careful optimization of the drying steps of the graphite furnace temperature program was essential to guarantee removal of most of the sample matrix and to obtain acceptable precision. All temperatures and times from steps 1 to 5 were exhaustively

investigated and adjusted to the optimum conditions, to prevent sample boiling and splashing. To improve drying efficiency, the sample was injected into the preheated tube at 90 °C under a slow injection rate, to facilitate matrix evaporation. This approach proved to be efficient in avoiding sample overloading. No significant analyte loss was observed.

### Cooling down step

Some authors have reported that the inclusion of a cool down step between the ashing and atomization cycles tends to lower background signals and to improve precision.<sup>18</sup> This approach was tested and did not show any significant improvement in the present application.

### Multivariate optimization

**Design 1.** Table 3 shows the experimental results in terms of the analyte signal (integrated absorbance) and the analyte/background signal ratio, together with coded and original values for the four variables of Design 1. The responses obtained at the twelve central point runs remained fairly stable, indicating that signal correction is not required.

**Table 4** Doehlert design for the second optimization step. The factors are the number of multiple injections ( $N$ ) and the volume of each sample injection ( $V_s$ ). The experiments were run in triplicate and in random order. Values in parentheses are coded factor levels.  $M$  = modifier volume. RSD = relative standard deviation of the analyte signal.  $f_v$  = volume correction factor (see text). The analyte and background signals were corrected by  $f_v$

Run	$N$	$V_s/\mu\text{L}$	$M/\mu\text{L}$	$f_v$	Corrected analyte signal (area, $\times 10^4$ )			Average signal ratio	RSD (%)
1	2 (0)	15 (-1)	2	34	7.71	7.38	5.41	0.44	18.17
8	3 (1)	25 (-0.5)	4	87	7.91	7.43	6.32	0.35	11.26
2	1 (-1)	25 (-0.5)	4	29	8.97	8.62	8.14	0.31	4.85
3	3 (1)	45 (0.5)	6	153	7.31	6.89	6.62	0.41	4.98
5	1 (-1)	45 (0.5)	6	51	8.25	7.06	7.41	0.37	8.11
6	3 (0)	55 (1)	8	189	6.98	6.41	5.65	0.30	10.54
4	2 (0)	35 (0)	5	80	8.24	7.25	7.11	0.32	8.15
7					7.56	6.95	6.24	0.34	9.59
10					6.55	6.53	6.08	0.27	4.18
9	3	35	5	120	6.28	6.24	5.88	0.32	3.66

A full quadratic model of the average analytical signal as a function of the coded factor levels was fitted by least squares to the data in Table 3, resulting in the expression

$$A_s = 0.163 - 0.080T_{\text{ash}} - 0.089T_{\text{ash}}^2 + 0.033M, \quad (1)$$

where only the statistically significant terms (at the 95% confidence level) are shown. The analysis of variance showed no evidence of a lack of fit for this model (Table 5).

A similar modeling with the analyte/background signal ratio as the response yielded

$$R_{a/b} = 0.517 + 0.246T_{\text{ash}} + 0.876t_{\text{ash}} - 0.446t_{\text{ash}}^2 + 0.644T_{\text{at}} + 0.511T_{\text{ash}}t_{\text{ash}} - 1.765T_{\text{at}}t_{\text{ash}} + 0.676T_{\text{at}}M \quad (2)$$

The number of significant terms doubled in relation to eqn. (1), and the analysis of variance present a significant lack of fit, as shown in Table 5.

To find the optimum conditions for the two responses, the critical points of eqns. (1) and (2) were searched using the Hessian formulation.<sup>35</sup> No maximum response, however, was found inside the experimental space defined by the factor levels of design 1. Both equations presented saddle points instead, and these were located slightly outside the region investigated. In coded levels, the critical points were calculated as follows:

$$A_s = 0.168, \text{ for } t_{\text{ash}} = -0.56, T_{\text{ash}} = -0.387, \\ T_{\text{at}} = -1.06^*, M = -0.610 \quad (3)$$

$$R_{a/b} = 0.240, \text{ for } t_{\text{ash}} = 0.482, T_{\text{ash}} = -0.604, \\ T_{\text{at}} = 0.502, M = -1.791^* \quad (4)$$

The asterisk indicates levels outside the experimental domain.

Saddle points are unsatisfactory, because they correspond to a minimum for some factors and at the same time to a maximum for the other factors. Even if maxima had been obtained in the present case, instead of saddle points, they would correspond to very different level combinations for the two responses, as shown by the above expressions. A compromise must therefore be sought.

Fig. 1 is a plot of the analyte/background signal ratio against the analyte signal. The results obtained in experiments 12, 18, 19 and 23 are not included, because they correspond to unacceptably low values for the analyte signal. As anticipated, there is no straightforward relation between the two responses. The best result for the signal ratio is that of run 13, while the highest analyte signal was obtained in run 3. The best settings, under these circumstances, should yield results close to the tip of the arrow, *i.e.* high  $A_s$  and  $R_{a/b}$  results. No single run is

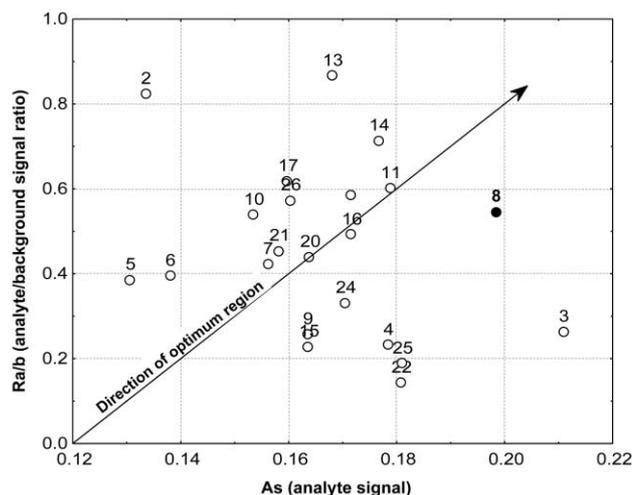


Fig. 1 Plot of the analyte/background signal ratio against the analyte signal. Data from Table 3. The full circle indicates the best overall experimental run.

entirely satisfactory, but a good compromise can be reached with the experimental settings of run 8, for which an average signal of 0.1985 was obtained together with a signal ratio of 0.54. The corresponding settings are as follows:

$$t_{\text{ash}} = 45 \text{ s}, T_{\text{ash}} = 1250 \text{ }^\circ\text{C}, T_{\text{at}} = 2436 \text{ }^\circ\text{C}, \\ M = 3582 \text{ mg L}^{-1} \quad (5)$$

For practical reasons, however, these settings were modified. To minimize analyte loss and provide suitable organic matrix removal, the ashing parameters were fixed at  $t_{\text{ash}} = 1200 \text{ }^\circ\text{C}$  and  $t_{\text{ash}} = 60 \text{ s}$ . Also, since a high modifier concentration tends to increase analyte retention in the graphite tube, possibly leaving some memory effect between successive determinations, a value of  $3000 \text{ mg L}^{-1}$  was adopted for  $M$ . Finally, if  $T_{\text{at}}$  is too low the peak shape becomes significantly distorted, affecting repeatability. An atomization temperature of  $2700 \text{ }^\circ\text{C}$  was chosen as a compromise. Additional experiments were run at and around these settings, confirming this choice was satisfactory, as shown in Table 6. The lower analyte signal values in the table, as compared to those in Table 3, are due to the use of a standard with a lower concentration ( $5.0 \text{ } \mu\text{g L}^{-1}$ ).

**Design 2.** Table 4 shows the results obtained in the experiments comprising the second Doehlert design. Quadratic models were fitted to each of the three responses (analyte signal, analyte/background signal ratio and analyte signal

Table 5 ANOVA results for the quadratic models fitted to the data from the first optimization step (Table 3)

Response: Analyte signal				
Source of variation	Sum of squares	Degrees of freedom	Mean square	F ratio
Regression	0.0525	14	0.00375	17.86
Lack-of-fit	0.00246	6	0.000410	1.95
Pure error	0.00105	5	0.000210	
Total	0.0560	25		
Response: Analyte/background signal ratio				
Source of variation	Sum of squares	Degrees of freedom	Mean square	F ratio
Regression	8.552	14	0.611	89.20
Lack-of-fit	1.984	6	0.331	48.32
Pure error	0.0343	5	0.00686	
Total	10.57	25		

**Table 6** Confirmatory experiments for Design 1 (results are the average of 8 replicates of a  $5.0 \mu\text{g L}^{-1}$  standard)

Experiment	1	2	3
$t_{\text{ash}}/\text{s}$	60	60	60
$T_{\text{ash}}/^\circ\text{C}$	1200	1200	1200
$T_{\text{at}}/^\circ\text{C}$	2700	2500	2900
$M/\text{mg L}^{-1}$	3000	3000	417
Analyte signal	0.0844	0.0691	0.0440
Signal ratio	0.58	0.52	0.32
RSD (%)	9.08	12.16	7.86

RSD), but no coefficient in any model proved to be statistically significant at the 95% confidence level. This seems to be mostly due to the relatively large extent of the pure error contribution to the overall variance. Nevertheless, the response surface fitted to the RSD values (Fig. 2) indicates that more precise signals are obtained at intermediate sampling volumes. Also, using three injections leads to a somewhat lower background signal. To obtain the best results, therefore, it is recommended to use 3 multiple injections of  $45 \mu\text{L}$  each.

**Method validation.** The analytical performance of the method proposed was evaluated with the standard validation tests, with results shown in Table 7.

Precision was evaluated from 20 replicates of a spiked naphtha sample. The observed Cochran coefficient and the ANOVA  $F$ -test value ( $C_{\text{observed}} = 0.462$  and  $F_{\text{observed}} = 2.11$ ) were both below the critical values at the 95% confidence level (0.598 and 3.06, respectively). The data set was therefore assumed to be homogeneous, and the overall relative standard deviation (RSD) was calculated and the obtained result (9.0%) was found to be below the maximum acceptable RSD (23.7%) defined by the Horwitz criterion at the concentration level used.<sup>34</sup>

Accuracy was assessed by spiking three naphtha samples. As shown in Table 8, good analyte recovery (81–104%) was obtained.

A remarkable linearity over the wide concentration range of  $0.5$  to  $120 \mu\text{g L}^{-1}$  was achieved (Fig. 3). The analytical curve obtained from eleven standards covering this range ( $y = 0.0091x - 0.0028$ ;  $r = 0.9987$ ) has a profile very similar to that of the analytical curve used for sample analysis in the  $0.5$ – $14 \mu\text{g L}^{-1}$  range ( $y = 0.008x + 0.0008$ ;  $r = 0.9980$ ). Additionally, the typical slopes of the analytical curve (0.008) and the analyte

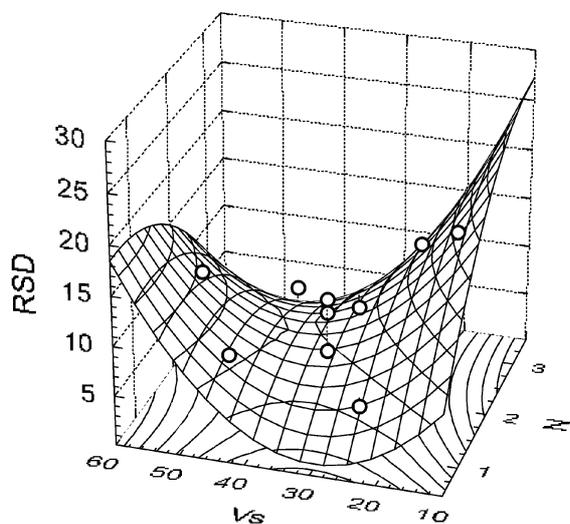
**Fig. 2** Response surface for the relative standard deviation (RSD) of the analyte signal as a function of the sample aliquot of each injection ( $V_s$ ) and the number of multiple injections ( $N$ ).**Table 7** Analytical figures of merit of the method for arsenic determination in naphtha by ETAAS using multiple injection and direct preconcentration

Figure of merit	
Analytical curve equation	$y = 0.008x + 0.0008$
Correlation coefficient, $r$	0.9980
Sensitivity <sup>a</sup> / $\mu\text{g L}^{-1}$	0.45
Limit of detection <sup>b</sup> / $\mu\text{g L}^{-1}$	0.49
Characteristic mass/pg	61
Linear working range/ $\mu\text{g L}^{-1}$	0.5–120
Relative standard deviation <sup>c</sup> (%)	9.0

<sup>a</sup>Calculated from the analytical curve as the minimum detectable concentration for an integrated absorbance of 0.0044. <sup>b</sup> $3s_{\text{blank}}$  criterion based on 10 replicates. <sup>c</sup>Measured from 20 replicates of a  $2.3 \mu\text{g L}^{-1}$  spiked sample.

**Table 8** Arsenic concentrations obtained in spiked naphtha samples

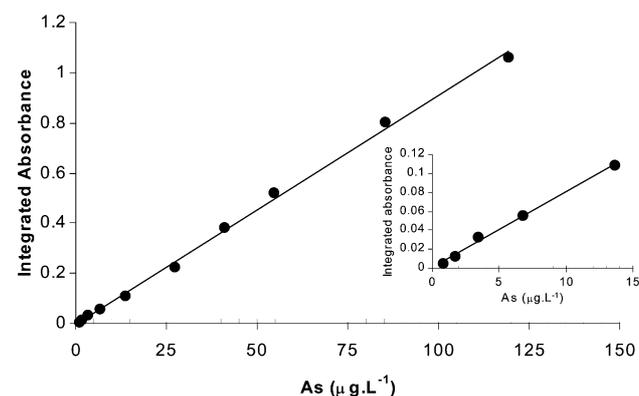
Sample	Added/ $\mu\text{g L}^{-1}$	Found/ $\mu\text{g L}^{-1}$	Expected/ $\mu\text{g L}^{-1}$	Recovery (%)
1	0	1.30		
	0.85	2.12	2.15	$98.5 \pm 3.9$
	1.36	2.48	2.66	$93.3 \pm 2.2$
	1.70	3.00	3.00	$99.9 \pm 0.7$
2	0	1.61		
	0.85	2.21	2.39	$92.6 \pm 8.7$
	1.70	3.37	3.24	$103.9 \pm 2.1$
	3.41	4.78	4.95	$96.7 \pm 1.4$
3	0	2.35		
	0.85	2.90	3.20	$89.8 \pm 5.5$
	1.70	3.28	4.05	$80.9 \pm 3.1$
	3.41	5.13	5.76	$89.0 \pm 2.8$

addition curves (0.0067, 0.008, 0.0091) do not differ significantly, indicating that matrix interference is negligible.

**Sample analysis.** Eleven naphtha samples taken from different lots were analyzed for arsenic, under the recommended analytical settings. The results are shown in Table 9. All arsenic amounts were found below  $3 \mu\text{g L}^{-1}$ . As already mentioned, most of the ETAAS analytical methods already developed are not suitable to such a low threshold.

## Conclusions

A simple and fast method for trace determination of arsenic in naphtha samples with direct preconcentration in the graphite tube was developed using electrothermal atomic absorption spectrometry with multiple injections and Zeeman-effect

**Fig. 3** Arsenic analytical curves.

**Table 9** Arsenic concentrations in Naphtha lots used at the Braskem petrochemical site in Brazil (NA = not available). Analysis performed at the optimized analytical settings (see text)

Sample	Sampling	Origin	Arsenic $\pm 1s/\mu\text{g L}^{-1}$
1	Storage tank	NA	1.30 $\pm$ 0.12
2	Ship	Brazil	0.97 $\pm$ 0.01
3	Storage tank	NA	2.15 $\pm$ 0.05
4	Ship	Argentina	0.94 $\pm$ 0.09
5	Ship	Brazil	2.30 $\pm$ 0.99
6	Ship	Brazil	0.59 $\pm$ 0.30
7	Ship	Morocco	1.58 $\pm$ 0.01
8	Ship	Algeria	1.41 $\pm$ 0.04
9	Ship	Algeria	2.89 $\pm$ 0.96
10	Ship	Brazil	2.53 $\pm$ 0.16
11	Ship	Algeria	1.53 $\pm$ 0.05

background correction. Naphtha samples were analyzed without any pretreatment, minimizing technician sample handling and allowing application in routine analysis. By using an organic standard and a suitable organic solvent the use of analyte addition technique was avoided and the analytical curve technique was applied for calibration. Quite low levels of arsenic were determined in eleven naphtha test samples, with concentrations ranging from 0.59 to 2.89  $\mu\text{g L}^{-1}$ .

The best experimental parameters were established by means of a multivariate approach based on Doehlert designs. With this procedure, the analyte signal and the precision were improved, and the background signal reduced. A remarkably low limit of detection and a very good sensitivity for arsenic determination in an organic matrix were thus obtained. Such figures of merit are comparable to that obtained by ICP-MS since it shows the advantage over the ICP-MS methods that no sample dilution is required. The performance of the method was evaluated with the standard statistical tools, with good results.

With minor adjustments to the graphite furnace program, the method can be adapted to analyze arsenic in other petroleum products (*e.g.*, gasoline, petroleum condensates). Preliminary studies along these lines are already being performed in our laboratory.

Finally, it is anticipated that improved performances can be obtained with different chemical modifiers. Palladium was chosen for the present application because of its good response to different elements, a convenience in industrial routine analysis.

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