

Behaviour of chemical modifiers in the determination of arsenic by electrothermal atomic absorption spectrometry in petroleum products

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Received 29 December 2004; received in revised form 9 February 2005; accepted 14 February 2005

Available online 19 March 2005

Abstract

Most comparative studies on the efficiency of chemical modifiers have been conducted in aqueous media. In the present work, we proposed a detailed study of the use of different chemical modifiers for direct determination of arsenic in complex organic matrices by electrothermal atomic absorption spectrometry (ETAAS). Palladium, rhodium, tungsten, silver, lanthanum and a mixture of palladium and magnesium were tested. The figures of merit used for evaluation and comparison were acquired in the optimal conditions for each modifier, established by multivariate optimization of the main variables based on Doehlert designs. Singular features were observed for the chemical behaviour of some modifiers in organic matrices compared to aqueous media, such as the worse performance of Pd + Mg modifier and no notice of severe tube corrosion from La application. Lanthanum was chosen as the best chemical modifier for the present application, according to predefined criteria. Lanthanum showed the minimum limit of detection, characteristic concentration and blank signal among all tested species and no effect of the concomitants usually present in petrochemical feedstocks. Using a 200 mg L⁻¹ lanthanum solution as a chemical modifier, the average relative standard deviations of 7 and 16% (at 3–15 µg L⁻¹ level) and characteristic concentrations of 0.47 and 0.77 µg L⁻¹ for naphtha and petroleum condensates, respectively, were observed.

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Keywords: Chemical modifier; Arsenic; Naphtha; Petroleum condensate; ETAAS; Doehlert

1. Introduction

Electrothermal atomic absorption spectrometry (ETAAS) has been widely used for determination of trace levels of arsenic in different matrices, including fuels and petroleum-derived samples [1–5]. However, the low performance of arsenic as an absorbing species and its high volatility make its determination a difficult task. The accurate quantification of arsenic is quite important in petrochemical industries because even traces present in the feedstock (naphtha or petroleum

condensate) can cause severe and irreversible catalyst poisoning [6].

Due to the high volatility of arsenic, the pyrolysis temperature in ETAAS analysis should be kept as low as possible to avoid analyte losses. However, the direct analysis of petroleum products requires sufficiently high pyrolysis temperatures to guarantee efficient matrix removal. Expressive losses of arsenic are observed in temperatures as low as 200 or 400 °C if no modifier is used [7–10] and, therefore, the use of chemical modification is mandatory for this application.

The amount of modifier used by different authors varies with each application, being usually in the 0.8–65 µg range when a solution of the modifier is used [7–17]. For arsenic determination, modifiers based on palladium have been gen-

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erally suggested. Comparative studies have recommended the use of palladium nitrate as a modifier for arsenic, either as such or mixed with magnesium nitrate, reaching pyrolysis temperatures from 1000 to 1400 °C [7,11–14,18]. Other species, such as rhodium [15,16], iridium [12,15], zirconium [8], thorium [8] and platinum [19] have also been recommended.

Since most comparative studies of the performance of chemical modifiers in the determination of arsenic have been conducted in aqueous medium, an extrapolation to organic systems would be inadequate. Furthermore, in most of these papers it is not clear if the data were obtained in the optimal conditions for each modifier. In the present work, we propose a detailed study of chemical modifier behaviour in complex organic matrices, such as petroleum products, after multivariate optimization of the main experimental conditions for each modifier based on Doehlert designs [20].

2. Material and methods

2.1. 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. 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.

2.2. Reagents and solutions

An 100 mg kg⁻¹ arsenic standard in mineral oil was supplied by Conostan (Conostan Oil Analysis Standards, Ponca City, OK, USA). All working standard solutions were prepared from this standard on a daily basis, using mixed xylenes (MX) as solvent to minimize changes in composition due to the samples volatility. MX is an internal Braskem product and its typical 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 were prepared in 0.1% (v/v) HNO₃ from a stock solution of 10,000 mg L⁻¹ Pd(NO₃)₂ in ca. 15% (v/v) HNO₃ (Merck, Darmstadt, Germany). La₂O₃, AgNO₃, Na₂WO₄·2H₂O, Mg(NO₃)₂·6H₂O, RhCl₃·3H₂O supplied by Merck were used to prepare the modifier solutions in 0.1% (v/v) HNO₃.

To study the effect of concomitants, different species were used: 99.8% (m/m) ethanol, 99.5% (m/m) pyridine, 99.5% (m/m) dichloromethane, 99% (m/m) heptahydrated zinc sulfate, 99% (m/m) potassium nitrate (Merck, Darmstadt, Germany), 99% (m/m) methanol, 99.5% (m/m) methyl-*tert*-butyl-ether (Braskem internal products), 99.9% (m/m)

carbon disulfide (JT Baker, USA), 98% (m/m) dibutyl disulfide (Aldrich, USA), 99% (m/m) sodium nitrate (Carlo Erba, Brazil), 1000 mg kg⁻¹ organometallic standard solutions of vanadium, nickel, silicon, phosphorus, copper, lead, iron and magnesium (Conostan, USA) and 1000 mg kg⁻¹ mercury organometallic standard solution (EM Science, Germany) were used. A small amount of ethanol was used in the preparation of stock solution of some inorganic salts, to help their solubilization in xylene.

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

2.3. Samples

All samples were collected in 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, deionized water and ethanol washings. This work was carried out at Braskem, a petrochemical plant located in northeastern Brazil. The samples were collected from the plant's raw material storage tank or directly from carrier ship tanks.

2.4. General analytical procedure

The naphtha sample and the modifier are injected at a rate of ca. 8.8 μL s⁻¹ into the graphite tube preheated at 90 °C, where preconcentration takes place. Three successive 45 μL sample aliquots are introduced in the tube. A 6 μL aliquot of the modifier solution is co-injected with the sample aliquot. The temperature is raised, leading to partial drying of each sample + modifier aliquot. The drying temperatures are carefully raised through each step to prevent sample sputtering due to high concentrations of volatile species in naphtha sample and also ensure removal of heavier compounds. At each multiple injection, the naphtha sample and modifier aliquots are dried following steps 1–4 described in Table 1, before the next injection. After the third injection, the temperature programme is completed according to the conditions shown in the table and the total amount of arsenic is determined from the integrated absorbance signal obtained for 2.8 s integration time. Following the stabilized-temperature platform furnace (STPF) concept [21], the same conditions for naphtha analysis, except for modifier concentration, pyrolysis and atomization temperatures, were used for all modifiers and sample analyses. The furnace programme used for petroleum condensate is also presented in Table 1, where each of the two multiple injections are dried until step 8 for arsenic preconcentration. In the temperature programme for naphtha, the furnace is cooled down to 90 °C in the step 4 to guarantee the introduction of the second and third injections of the volatile sample at the temperature defined by step 1. The cool down step was included at step 8 for the petroleum condensate analysis. Quite long time programmes were obtained as a result of the complex nature of the petroleum products and the large total sample

Table 1
Graphite furnace temperature programme for naphtha and petroleum condensate using lanthanum as chemical modifier

Cycle	Naphtha				Petroleum condensate			
	Step	Temperature (°C)	Time (s)	Argon flow (L min ⁻¹)	Step	Temperature (°C)	Time (s)	Argon flow (L min ⁻¹)
Drying (1–5 and 1–8)	1	90	2.0	3.0	1	90	2.0	3.0
	2	115	15.0	3.0	2	115	15.0	3.0
	3	120	10.0	3.0	3	122	25.0	3.0
	4	90	1.5	3.0	4	180	30.0	3.0
	5	180	20.0	3.0	5	280	25.0	3.0
					6	500	15.0	3.0
					7	500	3.0	3.0
					8	50	11.9	3.0
Pyrolysis (6–8 and 9–11)	6	800 ^a	10.0	3.0	9	800	30.0	3.0
	7	800 ^a	60.0	3.0	10	800	120.0	3.0
	8	800 ^a	2.0	0	11	800	2.0	0
Atomization (9–10 and 12–13)	9	2400 ^a	0.8 ^b	0	12	2400	0.8	0
	10	2400 ^a	2.0	0	13	2400	2.0	0
Cleaning/cooling (11–12 and 14–15)	11	2400	2.0	3.0	14	2400	2.0	3.0
	12	90	18.0 ^b	3.0	15	90	21.1	3.0

^a The pyrolysis and atomization temperatures were adjusted for each modifier by means of a multivariate optimization approach.

^b These settings were automatically adjusted for each modifier by the equipment depending on the pyrolysis and atomization temperatures for the minimum time to reach the required temperature.

volume injected into the tube for analyte preconcentration.

2.5. Optimization, evaluation and selection of chemical modifiers

Using a base method previously developed [5], the response of six different solutions of chemical modifiers (lanthanum, palladium, silver, rhodium, tungsten and a mixture of palladium and magnesium) was assessed, and also compared to the performance without a modifier. The critical variables (modifier concentration, pyrolysis temperature and atomization temperature) were optimized for each modifier. Therefore, the comparative analysis was performed based on the best results of each modifier. The methodology applied to acquire data for optimization and evaluation is presented in Table 2. All calculations were performed using the *Statistica* software package [22].

In the first step, the pyrolysis temperature was kept low enough (300 °C) to guarantee detection of any modification effect that could be masked at higher temperatures. The atomization temperature was fixed at 2700 °C to ensure arsenic atomization even if very stable species were formed between the element and the modifier.

In the next step, a Doehlert matrix [20,23] with 13 experiments was used for optimization. The pyrolysis temperature, considered the most critical variable, was assessed at seven levels. The atomization temperature and modifier concentration were each investigated at three levels. A plot of analytical signal against the ratio of the analytical to background signals was used to identify the best experiment. Experimental regions leading to high background signals were thus avoided,

and the region next to the chosen experiment was further investigated using the surface response for the analytical signal. To optimize the system without a modifier, the pyrolysis temperature was varied in five levels (200–1400 °C) and atomization temperature in three levels (2200–2800 °C). The system with the mixture of palladium and magnesium was submitted to a preliminary multivariable analysis in order to establish the concentration level of each species in the mixture and the best relation between them. The Pd concentration was varied at five levels (1–800 mg L⁻¹) and the Mg + Pd relation at three levels (5 + 1, 1 + 1 and 1 + 5). Then, the Mg + Pd relation was fixed at the optimum value and the total concentration of the species was varied near the optimum region with an additional Doehlert design.

The pyrolysis and atomization curves and analytical figures of merit were obtained for a straightforward comparison between the tested modifiers.

Each modifier was also assessed for the effect of concomitant species usually present in the naphtha and petroleum condensate samples. The concentration level of each species was defined based on the feedstock specification for petrochemical industries and typical results, as presented in Table 3. An arsenic standard solution was prepared in a xylene solution containing all concomitants while another standard solution was prepared in pure xylene. Both standard solutions were analyzed in four replicates with each modifier. The interference effect was evaluated using the *t*-test for comparison of the means, and was considered to be significant if the calculated *t*-value was higher than the critical one at 95% confidence level.

The best modifier for the present application was chosen according to the results of accuracy, precision, linearity and

Table 2
Methodology scheme applied to obtain data for modifier optimization and evaluation

Step	Aim	Conditions and comments	Final result
1—Initial screening on modifier concentration	Evaluate the effect of modifier concentration in the arsenic analytical signal	Arsenic standard = 120 $\mu\text{g L}^{-1}$ $T_p = 300^\circ\text{C}$ $T_a = 2700^\circ\text{C}$ Include blank analysis	Best modifier concentration range
2—Doehlert optimization	Establish optimum conditions for the main variables	Arsenic standard = 120 $\mu\text{g L}^{-1}$ $C_M =$ concentration range defined in the previous step $T_p = 300\text{--}1600^\circ\text{C}$ $T_a = 2200\text{--}2800^\circ\text{C}$ Random order Three replicates of central point for error estimate	Optimum conditions for main variables: C_M , T_p and T_a
3—Pyrolysis curve	Obtain the pyrolysis curve at optimum C_M and T_a	$C_M =$ optimum $T_p = 200\text{--}1600^\circ\text{C}$ $T_a =$ optimum	Pyrolysis curve
4—Atomization curve	Obtain the atomization curve at optimum C_M and T_p	$C_M =$ optimum $T_p =$ optimum $T_a = 1800\text{--}2800^\circ\text{C}$	Atomization curve
5—Analytical curve	Obtain the analytical curve at optimum conditions	Concentration range = 10–160 $\mu\text{g L}^{-1}$	Evaluation of linearity and sensitivity
6—Sample analysis	Evaluate the suitability of the method to real samples analysis	4 replicates (2 \times 2)	Confirmation of the suitability of the method to real samples analysis
7—Limit of detection	Calculate the limit of detection from blank analysis	10 replicates	Limit of detection
8—Precision and accuracy	Evaluate precision and accuracy from standard addition analysis to real sample	9 replicates (3 \times 3) Minimum acceptable R.S.D. is 16.7% according to Horwitz criterion	Relative standard deviation and recovery factor
9—Effect of concomitants	Evaluate the effect of concomitant species in the arsenic analytical signal	Analysis in 4 replicates of 20 $\mu\text{g L}^{-1}$ arsenic standard solutions prepared in presence and in absence of concomitant species usually present in naphtha	Effect of concomitants evaluation

C_M : modifier concentration, T_p : pyrolysis temperature and T_a : atomization temperature.

effect of concomitants. If all these figures of merit of the modifier are acceptable the modifier with the minima limit of detection or characteristic concentration should be selected.

3. Results and discussion

3.1. Methods optimization

The lanthanum modifier is taken as an example to illustrate how the optimization was performed. Firstly, from the initial screening (step 1 in Table 2), a significant improvement in the analyte signal was observed with lanthanum, compared to the analysis without modifier. Varying the modifier concentration in the range of 1–10,000 mg L^{-1} , the maximum analyte signal was observed around 100 mg L^{-1} lanthanum. Based on this result, the minimum and maximum levels of this variable in the Doehlert design were defined. The full experimental matrix is shown in Table 4, together

with the results obtained for the analyte signal (S_a) and background signal (S_b) of an arsenic standard. The ratio between those signals ($R_{a/b}$) was also calculated. Since the application of the Lagrange criteria to the quadratic model produced a saddle point, the most favourable conditions were searched for by evaluation of experimental results in a scatter plot of $R_{a/b}$ against S_a . This plot indicated that the conditions of experiment 9 provided the best results, particularly in terms of S_a . With the aid of the response surfaces, the region around these settings was further investigated and the optimum conditions were obtained (modifier concentration = 200 mg L^{-1} , pyrolysis temperature = 800 $^\circ\text{C}$ and atomization temperature = 2400 $^\circ\text{C}$). In these conditions, all further experiments were carried out to obtain quantitative data for modifier evaluation and comparison. The same approach was applied to the other modifiers and the final results are shown in Figs. 1–3 and Table 5. Each modifier is coded with the element's symbol and concentration. La200, for example, stands for 200 mg L^{-1} lanthanum solution.

Table 3
Composition of the solution used for interference study compared to typical and specification values for naphtha

Concomitant	Added concentration	Concomitant:arsenic relation ^a	Average level in naphtha	Naphtha specification
Sulfur (as carbon disulfide)	700 mg L ⁻¹	70000:1	120 mg L ⁻¹	350 mg L ⁻¹
Sulfur (as dibutyl disulfide)	700 mg L ⁻¹			
Nitrogen (as pyridine)	20 mg L ⁻¹	1000:1	1.6 mg L ⁻¹	5 mg L ⁻¹
Chloride (as dichloromethane)	16.3 mg L ⁻¹	815:1	1 mg L ⁻¹	5 mg L ⁻¹
Methanol	20 mg L ⁻¹	1000:1	3.8 mg L ⁻¹	10 mg L ⁻¹
Ethanol	400 mg L ⁻¹	20000:1	5.3 mg L ⁻¹	100 mg L ⁻¹
Methyl- <i>tert</i> -butyl-ether	240 mg L ⁻¹	12000:1	31.3 mg L ⁻¹	240 mg L ⁻¹
Copper	40 µg L ⁻¹	2:1	2 µg L ⁻¹	10 µg L ⁻¹
Lead	100 µg L ⁻¹	5:1	7.6 µg L ⁻¹	25 µg L ⁻¹
Iron	1200 µg L ⁻¹	60:1	34 µg L ⁻¹	300 µg L ⁻¹
Mercury	20 µg L ⁻¹	1:1	0.5 µg L ⁻¹	5 µg L ⁻¹
Vanadium	200 µg L ⁻¹	10:1	ND	ND
Nickel	200 µg L ⁻¹	10:1	ND	ND
Phosphorus	200 µg L ⁻¹	10:1	ND	ND
Magnesium	200 µg L ⁻¹	10:1	ND	ND
Silicon	200 µg L ⁻¹	10:1	ND	ND
Sodium	200 µg L ⁻¹	10:1	ND	ND
Potassium	200 µg L ⁻¹	10:1	ND	ND
Zinc	200 µg L ⁻¹	10:1	ND	ND
Sulfate	300 µg L ⁻¹	30:1	ND	ND

ND: not determined or not defined.

^a Related to 20 µg L⁻¹ arsenic standard.

Table 4
Three-variable Doehlert matrix—optimization of the system with lanthanum modifier

Order	C _M (mg L ⁻¹)	T _p (°C)	T _a (°C)	S _a (µA s)	S _b (µA s)	R _{a/b}
5	90 (0)	950 (0)	2500 (0)	0.3942	0.3762	0.0846
10	90 (0)	950 (0)	2500 (0)	0.3336	0.4168	0.079
14	90 (0)	950 (0)	2500 (0)	0.3906	–	0.1201
1	10 (–1)	950 (0)	2500 (0)	0.3698	0.2612	0.1083
4	50 (–0.5)	300 (–0.866)	2500 (0)	0.4555	0.4399	0.5406
8	50 (–0.5)	732 (–0.289)	2200 (–0.816)	0.3764	0.5545	0.159
6	170 (1)	950 (0)	2500 (0)	0.3934	0.3895	0.0574
11	130 (0.5)	1600 (0.866)	2500 (0)	0.2155	0.1852	0.029
3	130 (0.5)	1166 (0.289)	2800 (0.816)	0.2807	0.2592	0.0469
13	50 (–0.5)	1600 (0.866)	2500 (0)	0.2808	0.2564	0.0001
15	50 (–0.5)	1166 (0.289)	2800 (0.816)	0.534	0.4653	0.0581
7	90 (0)	516 (–0.577)	2800 (0.816)	0.6446	0.439	0.2828
12	130 (0.5)	300 (–0.866)	2500 (0)	0.4177	0.6498	0.6303
9	130 (0.5)	732 (–0.289)	2200 (–0.816)	0.6158	0.6036	0.1867
2	90 (0)	1383 (0.577)	2200 (–0.816)	0.2026	0.1703	0.0126

C_M: modifier concentration, T_p: pyrolysis temperature, T_a: atomization temperature, S_a: analyte signal (integrated absorbance), S_b: background signal, R_{a/b}: ratio between average analyte and background signals. Values in parentheses are dimensionless coded factor levels.

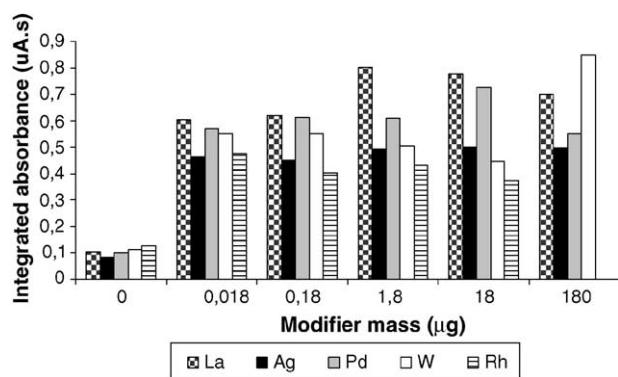


Fig. 1. Analytical signal of a 120 µg L⁻¹ arsenic standard solution in xylenes for different chemical modifiers (T_p = 300 °C and T_a = 2700 °C).

3.2. Evaluation and comparison of the modifiers

Fig. 1 demonstrates the significant effect of all modifiers on chemical modification of arsenic in the tested conditions. This result gives evidence of the need of chemical modification to improve the method's sensitivity. Due to the high cost of the reagent and decrease of the analytical signal with higher amounts of rhodium, the response of the system with 180 µg Rh was not tested. Additional blank analyses revealed that the higher analytical signals with tungsten, particularly with 180 µg of the modifier, may be assigned to reagent contamination. Therefore, the highest true analytical signal was in fact obtained with 1.8 µg lanthanum. An equivalent signal is found only with 18 µg palladium. Slightly different results could be observed in the optimized conditions for each mod-

Table 5
Summary of performance data of the evaluated modifiers

Modifier	Modifier concentration (mg L ⁻¹)	Modifier mass (µg)	Maximum pyrolysis temperature (°C)	Maximum atomization temperature (°C)	Limit of detection (µg L ⁻¹)	Characteristic concentration (µg L ⁻¹)	Analytical curve slope	Correlation coefficient	Blank signal (µA s)	Recovery factor (%)	Relative standard deviation (%)
Without modifier	–	–	200	2500	14.27	3.38	0.0013	0.9538	0.0157	130	7
La	200	3.6	800	2400	0.32	0.56	0.0078	0.9916	0.0017	118	6
Ag	1000	18	700	2100	3.22	1.33	0.0032	0.9995	0.002	88	11
Pd	3000	54	1500	2500	1.44	0.65	0.0060	0.9982	0.0318	112	17
Pd	100	1.8	1500	2500	0.71	1.04	0.0042	0.9945	0.0032	98	11
Rh	25	0.45	1300	2500	1.76	0.68	0.0065	0.9960	0.0139	90	13
W	10	0.18	1300	2500	0.92	0.79	0.0056	0.9947	0.0123	102	12
Pd+Mg	830+150	15+2.7	1100	2600	1.6	0.86	0.0051	0.9991	0.0223	93	12

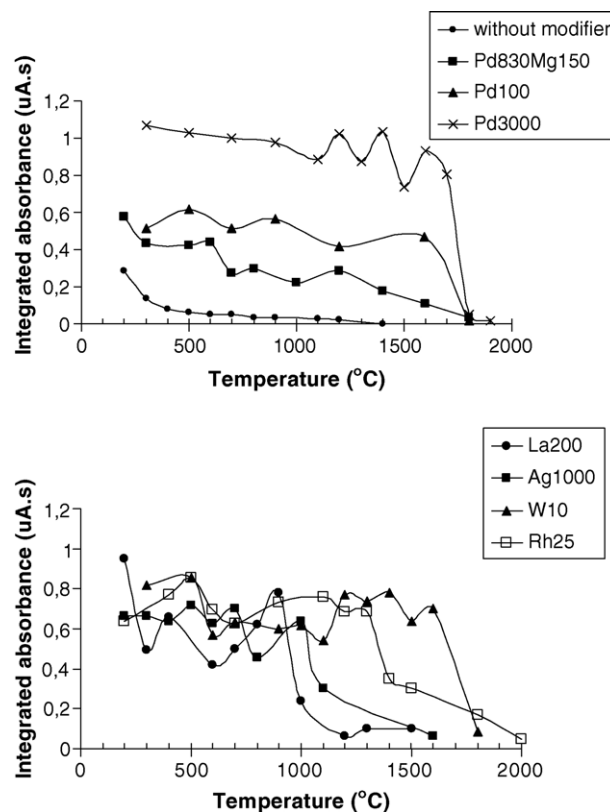


Fig. 2. Pyrolysis curves of tested modifiers at optimized conditions.

ifier. Therefore, this variable was further investigated with a Doehlert design.

Table 5 shows all quantitative results obtained for evaluation of each modifier and comparative analysis. The modifier concentration, pyrolysis temperature and atomization temperature, optimized from multivariate Doehlert designs, are presented in the table. All modifiers showed excellent linearity, demonstrated from the correlation coefficients presented in Table 5. La200 showed the highest slope of the analytical curve, among all modifiers. As a result of the highest sensitivity, this modifier presented the lowest characteristic concentration. Ag1000 and Pd100 showed the lowest sensitivities. The statistically significant difference between these slopes was confirmed by 95% confidence intervals calculated for each slope.

Fig. 2 shows the pyrolysis curve for each modifier at optimized conditions. Pd100, Pd3000 and W10 led to the highest analyte stabilization, allowing the use of high pyrolysis temperatures without significant arsenic losses. More significant losses are only observed at a temperature level superior to 1600 °C. The uppermost analytical signals were obtained with Pd3000. Pd100 presented a more stable profile along a plateau, compared to the quite irregular profile of the other modifiers. La200 and Ag1000 presented the lowest ideal pyrolysis temperatures (lower than 1000 °C), although such temperatures are high enough to accomplish effective sample ashing. All modi-

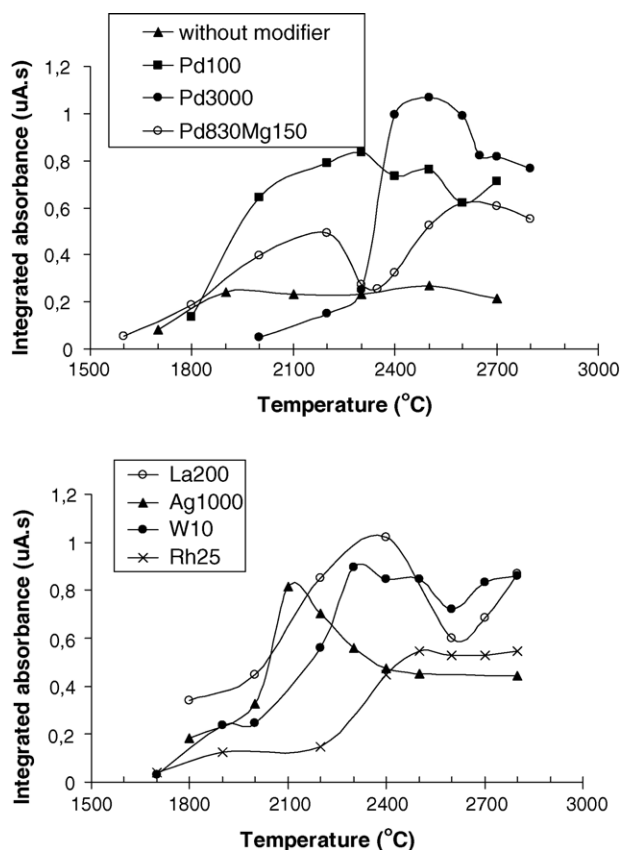


Fig. 3. Atomization curves of tested modifiers at optimized conditions.

fiers showed better results than the system without a modifier.

The atomization profile of each modifier solution is shown in Fig. 3. Arsenic atomization starts around 1700 °C for all modifiers except La200 and Pd3000. At this temperature La200 already provides a significant analyte signal while the atomization in the system modified with Pd3000 only initiates above 2000 °C. With Rh25 and Pd3000, more stabilized As species seems to be formed since higher temperatures (above 2500 °C) are needed to guarantee effective atomization of the analyte. Among the tested species, Ag1000 provided the lowest atomization temperature, around 2100 °C. La200 and Pd3000 showed the highest analyte signals in their ideal atomization temperatures despite their differences in pyrolysis profiles. Such result demonstrates the effectiveness in the analyte stabilization, matrix removal and atomization for both modifiers regardless the difference in their pyrolysis temperatures. The lowest analytical signals were obtained with Rh25 and Pd830Mg150.

The presence of magnesium in the mixture with palladium reduced the analytical signal and the maximum pyrolysis temperature compared to the solutions containing only palladium. The mixture Pd830Mg150 did not show a satisfactory stabilization profile, with significant arsenic losses around 600 °C. The mixture of palladium and magnesium also showed an irregular atomization behaviour, with partial

atomization around 2200 °C and a more effective one at about 2600 °C. Qiao and Jackson [24] suggested a physical nature of magnesium activity, playing a role in the homogeneous distribution of palladium during pyrolysis stage. Pszonicki and Dudek [10] also pointed the effect of magnesium itself, as an independent modifier. The dip in the atomization curve for Pd830Mg150, similar to the initial drop in pyrolysis curve, may be caused by formation of two different As-modifier species, possibly confirming the hypothesis of Pszonicki and Dudek.

The best result for palladium, using 3000 mg L⁻¹, required the highest amount of modifier among the tested species. The smallest amount of modifier (0.18 µg) was required with tungsten. The amount of each modifier necessary for best performance is shown in Table 5.

The lowest limit of detection (0.32 µg L⁻¹) was observed with La200 as the modifier. On the other hand, Ag1000 provided the highest values for this parameter. Although higher values were observed for the other modifiers, compared to La200, these limits of detection (from 0.72 to 1.76 µg L⁻¹) are still quite good. The optimization process carried out for each modifier is probably the reason of such performance.

The blank signal was kept quite low, especially with La200, Ag1000 and Pd100 as modifiers. As already mentioned, tungsten showed high blank signals when higher amounts of the modifier were used, although a low blank signal was observed at the optimized conditions.

Comparing the results obtained for 20 µg L⁻¹ arsenic standard, Rh25 provided the lowest background signal and the highest signal/background ratio ($R_{a/b}$). Pd3000 also showed high $R_{a/b}$, followed by La200. Since the background signal without modifier was almost ten times higher than the average obtained with all modifiers, it is evident that the use of a chemical modifier leads to an expressive reduction of the background signal, because higher pyrolysis temperatures can be applied.

All modifiers showed satisfactory recovery factor and relative standard deviation, as presented in Table 5. Therefore, there is no evidence of lack of precision or accuracy of the method for any modifier.

In the effect of concomitant species study, each pair of results was assessed by a *t*-test. Pd100, Ag1000 and W10 showed a statistically significant difference between the average analyte signals obtained from solutions with and without concomitants. The presence of interfering species led to an increase in the analytical signal of 84% (Pd100), 136% (Ag1000) and 146% (W10). Since the tested species are usually present in real samples, the use of such modifiers would lead to false positive results. The other modifiers were not affected by the concomitant species. It is worth noticing that a higher amount of palladium is required to avoid the influence of other species in the analyte signal, since either Pd3000 or Pd830Mg150 did not show any interference effect.

From the results presented previously, one can observe the addition of magnesium to the palladium solution caused the deterioration of the method performance. In aqueous me-

dia, the introduction of magnesium is usually recommended to improve the method sensitivity. The activity of magnesium as chemical modifier may be related to presence of certain amount of nitrate ions as observed by Pszonicki and Dudek [10]. Thus, the addition of magnesium does not improve the behaviour of the palladium modifier in the analysis of hydrocarbon-based matrices.

The results for palladium were quite similar to the commonly observed in aqueous media, leading to excellent results, particularly in terms of method sensitivity. However, the very strong interaction between the modifier and the analyte required high atomization temperatures leading to rapid tube degradation. On the other hand, lanthanum behaved in the opposite way since the severe tube corrosion observed in aqueous systems was not noticed in the present application.

3.3. Selection of the best modifier for the present application

Based on the previous results, 200 mg L⁻¹ lanthanum was selected as the best modifier for the present application. Only Pd100, Ag1000 and W10 were excluded from the analysis because of their susceptibility to the presence of concomitants. Therefore, lanthanum was chosen among the remaining species because of its best limit of detection and characteristic concentration.

Although the pyrolysis temperature recommended for lanthanum application was lower than for other modifiers, the low background signal, the high method sensitivity and the absence of the interfering effect of the concomitant species demonstrate the suitability of this temperature to the present application.

The interaction between arsenic and lanthanum, producing stable compounds such as LaAs₂, LaAs and La₄As₃, was observed by Babizhetskyy et al. [25]. In addition, La(III) has been used by different authors in the separation, preconcentration and removal of arsenic species in aqueous medium at µg L⁻¹ level [26–28]. The interaction between La(III) and As(III) was also employed in the spectrophotometric determination of lanthanum with reagents based on arsenic (arsenazo III [29], arsenazo-*p*-NO₂ [30] and arsenazo M [31–33]). The arsenic-based group, present in these reagents as a substituent in the aromatic ring, reacts with lanthanum giving a coloured complex.

However, despite the success of the application of La–As interaction to different systems, lanthanum has been rarely used as modifier in ETAAS. Bermejo-Barrera et al. [11,17] did not observe a good performance of La(III) as a chemical modifier for quantifying arsenic in seawater by ETAAS. This result might be explained by the possible corrosion of the graphite tube by the formation of acetylene in gaseous phase and also because lanthanum was used in its chloride form. It is well known that lanthanides form carbides, which are hydrolyzed to acetylene, leading to corrosion of the graphitic surface and a consequent drop in sensitivity [34]. Moreover,

the use of La in its chloride form can also play a role in the arsenic atomization mechanism. Slaveykova et al. [7] and Pszonicki and Dudek [10] observed significant differences in arsenic stabilization when palladium was applied as nitrate or chloride. Analyte losses, particularly of the organometallic species, were noticed when PdCl₂ was used as a modifier. According to the authors, the formation of volatile species from reaction between chloride and the analyte was the reason for such behaviour. Another reason could be the formation of intercalated compounds of chloride and palladium in the graphitic structure, in which arsenic would bind and reduce the method's sensitivity, as mentioned by Bulska and Ortner [35]. Such effects may also occur when LaCl₃ is used. Therefore, the use of La₂O₃ and a non-aqueous medium in the present work may justify the greater efficiency of lanthanum for this application compared to the data available in the literature.

3.4. Method validation

The analytical performance of the methods proposed here was evaluated with standard validation tests at the best settings found in the optimization study, with results shown in Table 6.

The methods accuracy was assessed by spiking naphtha and petroleum condensate samples in the 2–10 µg L⁻¹ range. Good analyte recoveries, in the range of 89–108%, were obtained. Sample spiking was used for accuracy assessment since a standard reference material is not available in a suitable matrix such as naphtha, xylene, toluene or light oil at the working concentration range. Additionally, there is no standard method (e.g. ASTM) for arsenic determination in petroleum products at this concentration level available for comparison.

Precision was assessed with a spiked sample in two concentration levels. The solutions were analyzed five times in four replicates, and the relative standard deviations (R.S.D.s)

Table 6
Analytical figures of merit of the method for arsenic determination in naphtha and petroleum condensate by ETAAS using lanthanum as chemical modifier

Figure of merit	Naphtha	Petroleum condensate
Analytical curve equation	$Y = 0.0093x - 0.0016$	$Y = 0.0057x - 0.0062$
Correlation coefficient (<i>r</i>)	0.9980	0.9984
Characteristic concentration ^a (µg L ⁻¹)	0.47	0.77
Limit of detection ^b (µg L ⁻¹)	0.56	1.33
Characteristic mass (pg)	63.5	69.3
Linear working range (µg L ⁻¹)	0.56–150	1.33–180
Relative standard deviation (%)	6 ^c –8 ^d	14 ^c –19 ^d

^a Calculated from the analytical curve as the minimum detectable concentration for an integrated absorbance of 0.0044.

^b 3_Sblank criterion based on 10 replicates of a sample at concentration level near blank.

^c Measured from 20 replicates of a 15 µg L⁻¹ spiked sample.

^d Measured from 20 replicates of a 3 µg L⁻¹ spiked sample.

were calculated from the 20 absorbance signals and compared to the maximum acceptable R.S.D.s as given by the Horwitz criterion for intralaboratory studies at those concentration levels [36]. In the 1–5 $\mu\text{g L}^{-1}$ range, the maximum limit is 23.7%, while in the 10–50 $\mu\text{g L}^{-1}$ range it is 16.7%. The obtained results were found to be below the maximum acceptable R.S.D.

A remarkable linearity over a wide concentration range of 0.5–180 $\mu\text{g L}^{-1}$ was achieved. The confidence interval of the intercepts include zero and, therefore, one can assume that the analytical curves pass through the origin, that is, they are unbiased. Matrix interference was also investigated by comparing the slopes of the analytical curve in xylenes and the analyte addition curve, according to statistical procedures suggested by Massart [37]. The slopes difference was confirmed to be non-significant by applying a *t*-test, in which the t_{observed} (0.007 and 0.369) were inferior to the t_{critical} (2.776 and 3.182, respectively) at the 95% confidence level. These results confirm the possibility of using the direct calibration method instead of the laborious standard addition method for routine sample analysis.

In a tube lifetime study, a freshly prepared 50 $\mu\text{g L}^{-1}$ arsenic standard was successively analyzed until some sign of deterioration of either the tube walls or the analytical signal was observed. The system showed a great performance for the organic system modified with lanthanum. Although best results were observed at up to ca. 150 firings, the tube could be used in up to 510 firings without any sign of deterioration in the method sensitivity. This limit was established by a fault alarm displayed by the equipment, probably due to the degradation of the tube walls. Typical limits of 200 or 300 firings were usually observed in our laboratory when working with organic matrices and other modifiers.

Table 7
Arsenic concentrations in naphtha and petroleum condensate lots used at the Braskem petrochemical site in Brazil

Sample	Product	Origin	Arsenic $\pm 1s$ ($\mu\text{g L}^{-1}$)
1	Naphtha	Brazil	1.84 \pm 0.05
2	Naphtha	Brazil	1.69 \pm 0.10
3	Naphtha	Brazil	1.66 \pm 0.06
4	Naphtha	Brazil	1.67 \pm 0.17
5	Naphtha	Brazil	1.49 \pm 0.26
6	Naphtha	Lybia	1.62 \pm 0.20
7	Naphtha	Algeria	1.16 \pm 0.18
8	Naphtha	Algeria	1.51 \pm 0.10
9	Naphtha	Algeria	1.28 \pm 0.09
10	Naphtha	Syria	1.54 \pm 0.06
11	Naphtha	Brazil	2.52 \pm 0.01
12	Naphtha	Brazil	2.02 \pm 0.03
13	Naphtha	Brazil	0.92 \pm 0.07
14	Petroleum condensate	Algeria	2.85 \pm 0.27
15	Petroleum condensate	Algeria	3.26 \pm 0.53
16	Petroleum condensate	Algeria	2.05 \pm 0.32
17	Petroleum condensate	Algeria	2.64 \pm 0.21
18	Petroleum condensate	Algeria	1.75 \pm 0.17

Analysis performed at the optimized analytical settings with lanthanum (see text).

3.5. Sample analysis

Eighteen naphtha and petroleum condensate samples taken from different lots were analyzed for arsenic, under the recommended analytical settings. As presented in Table 7, all arsenic amounts were found below 5 $\mu\text{g L}^{-1}$ a value still acceptable in terms of catalyst poisoning.

4. Conclusions

Original data on chemical modifiers' behaviour on the determination of arsenic in petroleum products were obtained, from which lanthanum showed the best performance and, therefore, was chosen for the present application. The results clearly indicated some differences in the modifiers' behaviour in organic medium compared to the results obtained by other authors in aqueous medium.

The best experimental conditions of the main parameters were established by means of a multivariate approach based on Doehlert designs. With this procedure, the optimum response for each modifier could be used for comparison.

Although lanthanum has been almost banned from ETAAS modifiers lists, we proved by comprehensive data the advantages of using such element as chemical modifier with organic matrices. Such behaviour has been continuously confirmed in our lab in Braskem by routine analysis of naphtha and petroleum condensate, where other metal (e.g. lead) are also determined with lanthanum.

The analytical method developed using lanthanum as the chemical modifier was demonstrated to be suitable for arsenic determination in naphtha and petroleum condensate in trace levels.

Acknowledgements

The authors thank Braskem S.A, CTPETRO and CNPq for material and financial support of the work reported here.

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