Original Paper

Application of multivariate techniques for optimization of direct method for determination of lead in naphtha and petroleum condensate by electrothermal atomic absorption spectrometry

Fabio de S. Dias[1], **Walter N. L. dos Santos**[1,2], **Antônio C. S. Costa**[1], **Bernhard Welz**[1,3], **Maria Goreti R. Vale**[4], and **Sérgio L. C. Ferreira**[1,*]

[1] Instituto de Química, Universidade Federal da Bahia, Salvador, Bahia 40170-290, Brazil
[2] Departamento de Ciências Exatas, Universidade Estadual de Santa Cruz, Campus Soane Nazaré de Andrade, Ilhéus, Bahia CEP-45662-000, Brazil
[3] Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil
[4] Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS 91501-970, Brazil

Abstract. A direct method is proposed for the determination of lead in naphtha and petroleum condensate by electrothermal atomic absorption spectrometry (ET AAS) using palladium as a permanent modifier. The procedure includes the dilution of 3 mL of sample (naphtha or petroleum condensate) to a final volume of 10 mL with xylene, and direct injection of 30 μL of this solution into the graphite furnace. The optimization of the instrumental conditions was performed using multivariate techniques. Firstly, a 2^3 full factorial design was performed for preliminary evaluation of the factors: pyrolysis time, pyrolysis temperature and atomization temperature. This experiment showed that in the studied levels only the factors pyrolysis time and atomization temperature were significant. Then, a 3^2 full factorial design was performed for the determination of the critical conditions of these variables. The method allows the determination of lead using the standard calibration technique with a calibration curve from 2.6 to 30 μg L^{-1} (correlation coefficient higher than 0.998). A limit of detection (3σ) of 0.8 μg L^{-1} and a characteristic mass of 35 pg were obtained in the presence of palladium as modifier. The precision expressed as relative standard deviation (RSD) was 1.5 and 0.8% for lead concentrations of 3.0 and 30 μg L^{-1} ($n = 10$). Recovery studies demonstrate that lead can be determined in naphtha and petroleum condensate using calibration with organic standard solutions. This method was applied for the determination of lead in three petroleum condensate and two naphtha samples. The concentrations found for the petroleum condensate was between 2.7 and 5.7 μg L^{-1}, while the naphtha samples did not contain any detectable lead.

Key words: Lead; naphtha; petroleum condensate; ET AAS.

Lead and some other metals are often determined in petroleum and its derivatives [1, 2]. However, the digestion step of these samples is normally very complicated. The analytical techniques that allow direct analysis are obviously preferred because their digestion is usually quite complicated [3–8] and includes the risk of loss of volatile analytes, such as lead. Reyes and Campos [9] proposed a method for the determination of lead in diesel and gasoline samples using electrothermal atomic absorption spectrometry (ET AAS). Kowalewska et al. [10] investigated organic

---

* Author for correspondence. E-mail: slcf@ufba.br

palladium and palladium–magnesium as chemical modifiers for the direct determination of lead in fractions from petroleum distillation by ET AAS. A method using filter furnace ET AAS was proposed for determination of lead and other elements in gasoline and diesel fuel samples [11], however this technique is not generally available. Nakamoto [12] proposed a fast procedure for the determination of lead in thermally cracked gasoline by ET AAS. The same technique was also proposed by Campos et al. [13] for the determination of lead in gasoline based on a three-component solution. Turunen et al. [14] used complete digestion with a mixture of nitric and sulfuric acid prior to the determination of lead and other metals in heavy oil samples by ET AAS. Inductively coupled plasma mass spectrometry (ICP-MS) has also been proposed for the determination of lead, nickel and vanadium in crude petroleum from Saudi Arabia [15]. Another method based on ICP-MS used introduction of samples in the form of micro emulsions for determination in lead and cadmium in petroleum products [16].

Multivariate chemometric techniques have been applied increasingly for the optimization of analytical procedures during the last years [17, 18]. The two-level full factorial design is often used for preliminary evaluation of the factors of the process [19–23], and response surface methodologies (RSM), such as central composite, Box-Behnken, Doehlert matrix and the three-level full factorial design are typically used for the determination of the critical conditions of these factors [17, 24]. However, among these RSM, the three-level full factorial design has been used only infrequently, because it requires a relatively large number of experiments if the factor number is higher than 2 [24, 25].

In the present paper a direct method for determination of lead in naphtha and petroleum condensate samples by ET AAS is proposed, using palladium nitrate as permanent modifier. The method is based on direct injection of the diluted sample solution into the graphite furnace and calibration against standards prepared from an organometallic stock solution. The optimization was carried out using two-level and three-level full factorial designs.

Experimental

Apparatus

All experiments were carried out using a Varian Model Spectra AA220Z electrothermal atomic absorption spectrometer with

Table 1. Temperature program for lead determination using Pd as permanent modifier

Cycle	Step	Temp/°C	Time/s	Ar flow rate/L min^{-1}
Drying	1	85	5.0	3.0
	2	95	40.0	3.0
	3	120	10.0	3.0
Pyrolysis	4	750	10.0	3.0
	5	750	10.0	3.0
	6	750	2.4	3.0
Atomization	7	2270	1.0	0.0
	8	2270	2.0	0.0
Cleaning	9	2500	2.0	3.0

Zeeman-effect background correction, equipped with a Model PSD 100 auto sampler. Argon 99.998% (White Martins, Brazil) was used as the purge gas. The lead hollow cathode lamp (Varian) was operated with a current of 4.0 mA, and the analytical line at 283.3 nm was used with a spectral bandwidth of 0.5 nm. Pyrolytic graphite coated graphite tubes with integrated platforms (Varian) were used throughout, using a volume of 30 µL of sample or calibration solution throughout. Instrumental parameters and operational conditions were those recommended by the manufacturer. Integrated absorbance (peak area) was used for signal evaluation exclusively. The graphite furnace temperature program is shown in Table 1.

Application of the permanent modifier

The treatment of the integrated platform with palladium nitrate was performed by applying 20 µL of a 1000 mg L^{-1} Pd solution (as the nitrate) onto the platform and submitting the tube to the temperature program proposed previously [26], which is shown in Table 2. This procedure was repeated 13 times in order to obtain a final deposit of 260 µg of palladium as a permanent modifier.

Reagents and solutions

The oil base lead standard of 1000 mg kg^{-1} was supplied by Conostan (Conostan Oil Analysis Standards, Ponca City, OK, USA). Lead stock standard solution of 1000 µg L^{-1} was prepared using xylene (Merck, Darmstadt, Germany) as solvent. A palladium stock solution of 1000 mg kg^{-1} (Merck, Germany) was used to apply the permanent chemical modifier.

Table 2. Temperature program for the treatment of the integrated graphite platform with palladium as permanent modifier

Step	Temp/°C	Time/s	Ar flow rate/L min^{-1}
1	90	15.0	2.0
2	250	35.0	2.0
3	250	6.0	0.0
4	1000	5.0	0.0
5	1000	5.0	0.0
6	1000	1.0	0.0
7	2000	2.5	0.0
8	2000	2.5	0.0
9	2000	0.5	2.0

Samples and sample preparation

The samples of petroleum condensate and naphtha were collected from raw material storage tanks in clean borosilicate bottles and stored at $4\,^\circ$C prior to the analysis, which usually was performed within three days. The cleaning process of sampling apparatus involved nitric acid and water washings and drying in an oven at $100\,^\circ$C. The sample solutions of naphtha and petroleum condensate were prepared by diluting 3 mL of sample to 10 mL using xylene.

Optimization strategy

Drying time, drying temperature, cleaning stage and gas flow were fixed as recommended by the instrument manufacturer as shown in Table 1. The optimization of the other conditions was carried out in two steps. Firstly, a 2^3 full factorial design involving the factors: pyrolysis time and temperature and atomization temperature was performed. Afterwards a 3^2 full factorial design was carried out for the determination of the optimum conditions of pyrolysis time and atomization temperature. In both factorial designs $30\,\mu$L of xylene solution were used containing $100\,\mu$g L^{-1} lead, and palladium was used as permanent modifier. Triplicates of central point were performed for evaluation of experimental error. In both designs, the analytical response was integrated absorbance (peak area). The experimental data were processed using the STATISTICA computer program [27].

Results and discussion

Optimization of the instrumental conditions

The determination of the critical conditions pyrolysis time and temperature and atomization temperature was carried out in two steps. Firstly, a 2^3 full factorial design was performed; the pyrolysis time was varied from 15 to 30 s, the pyrolysis temperature from 500 to $1000\,^\circ$C and the atomization temperature from 2000 to $2400\,^\circ$C. The results of this design, with integrated absorbance as response, are shown in Table 3. The evaluation of this experiment demonstrated that only the factors pyrolysis time and atomization temperature

are significant, as can be seen in the Pareto chart in Fig. 1. Usually in ET AAS the pyrolysis temperature is one of the most critical parameters, at least for the more volatile elements such as lead. The fact that this factor was found not to be significant in this optimization indicates that the organic matrix can apparently be removed to a great extent already at $500\,^\circ$C, and that no lead is lost in the presence of the palladium modifier at least up to $1000\,^\circ$C. An intermediate pyrolysis temperature of $750\,^\circ$C was therefore chosen for all future experiments. The positive values for the effects of pyrolysis time and atomization temperature indicated that in the studied levels, the absorbance increased with increasing of these factors.

Considering that, a 3^2 full factorial design was performed for the determination of the optimum conditions for the factors pyrolysis time and atomization temperature. The matrix of the design and the results are summarized in Table 4.

The below equation illustrates the relation between pyrolysis time (Pyt), atomization temperature (AT) and analytical signal (AS), considering the real values.

$$AS = -6.54 + 0.041(\text{PyT}) + 0.006(\text{AT})$$
$$- 2.94 \cdot 10^{-4}(\text{PyT})^2 - 1.16 \cdot 10^{-5}(\text{PyT})(\text{AT})$$
$$- 1.17 \cdot 10^{-6}(\text{AT})^2$$

This equation shows a critical point in the surface response, which is a maximum for the pyrolysis time of (24.3 s) and for the atomization temperature of ($2263\,^\circ$C). The way of calculating these critical points has been published in previous papers [6, 17, 19].

The fact that the pyrolysis time is of importance, while the pyrolysis temperature is not, can only be explained by the gas flow regime in the graphite furnace

Table 3. Matrix of the two-level factorial design

Experiment	Pyrolysis time/s	Pyrolysis temperature/$^\circ$C	Atomization temperature/$^\circ$C	Analytical signal/s
1	10 (−1)	500 (−1)	2000 (−1)	0.1016
2	30 (1)	500 (−1)	2000 (−1)	0.1296
3	10 (−1)	1000 (1)	2000 (−1)	0.0947
4	30 (1)	1000 (1)	2000 (−1)	0.1145
5	10 (−1)	500 (−1)	2400 (1)	0.2040
6	30 (1)	500 (−1)	2400 (1)	0.2313
7	10 (−1)	1000 (1)	2400 (1)	0.2009
8	30 (1)	1000 (1)	2400 (1)	0.2449
9 (C)	15 (0)	750 (0)	2200 (0)	0.1820
10 (C)	15 (0)	750 (0)	2200 (0)	0.1888
11 (C)	15 (0)	750 (0)	2200 (0)	0.1812

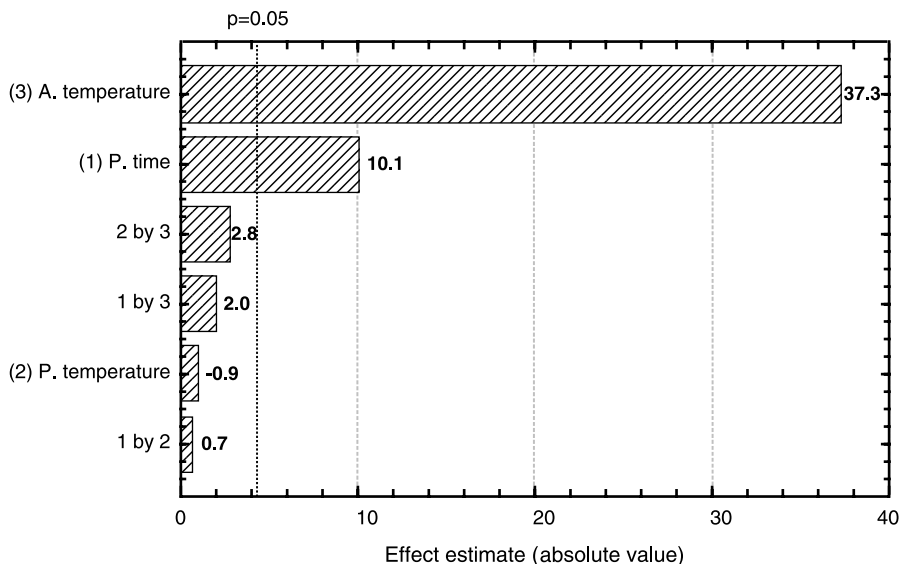A $30\,\mu$L of lead solution of concentration $100\,\mu$g L^{-1}.

p=0.05

Fig. 1. Pareto chart – instrumental factors for the determination of lead using ET AAS

Table 4. Matrix of the three-level factorial design

Experiment	Pyrolysis time/s	Atomization temperature/°C	Analytical signal/s
1	22.5 (0)	2400 (+1)	0.2180
2	30.0 (+1)	2000 (−1)	0.2033
3	15.0 (−1)	2000 (−1)	0.1277
4	15.0 (−1)	2200 (0)	0.1791
5	30.0 (+1)	2400 (+1)	0.1998
6	22.5 (0)	2000 (−1)	0.1352
7	30.0 (+1)	2000 (−1)	0.1441
8	15.0 (−1)	2400 (+1)	0.2216
9	22.5 (0)	2200 (0)	0.2538
10	22.5 (0)	2200 (0)	0.2424
11	22.5 (0)	2200 (0)	0.2440

A 30 μL of lead solution of concentration 100 μg L^{-1}.

Table 5. Calibration equations and correlation coefficients for determination of lead in petroleum derivatives

Calibration	Equation	Correlation coefficient
Analytical curve using organic standards	$Y = 0.0025 * C_{Pb} + 0.0015$	0.999
Analyte addition technique in naphtha	$Y = 0.0024 * C_{Pb} + 0.0008$	0.998
Analyte addition technique in petroleum condensate	$Y = 0.0024 * C_{Pb} + 0.0042$	0.998

used for the experiments. As the system does not have separate controls for external (protective) and internal (purge) gas flows, a relatively long time is apparently required to remove the vaporized organic matrix from the absorption volume.

Analytical features

The calibration curves for lead using organic standards in xylene showed a linear response from 2.6 to 30 μg L^{-1} with a correlation coefficient of 0.998. The precision calculated from ten consecutive measurements and defined as the relative standard deviation (RSD) of solutions containing 3.0 and 30 μg L^{-1} of lead were 1.5 and 0.8%, respectively. The limit of detection (LOD), defined as the lead concentration that gives a response equivalent to three times the standard deviation of the blank ($n = 10$), was found to be

0.8 μg L^{-1}. The characteristic mass was determined as 35 pg. The calibration equation is shown in Table 5. Experiments involving the analyte addition technique using organic standards were also performed for samples of naphtha and petroleum condensate. The calibration equations for each sample are also shown in Table 5; the evaluation of these data shows that the slopes of the calibration curves using standard calibration and the analyte addition technique for the real samples are very similar. This means that lead can be determined in naphtha and petroleum condensate samples directly using the standard calibration technique with organic standards.

Determination of lead in petroleum derivatives

Petroleum condensate is a fraction of petroleum comprised of some thousand hydrocarbon compounds in the range of 2–25 carbon number, with a distillation range usually from 30 to 330 °C and a relative density of 0.71. It is used as feedstock for petrochemical

Table 6. Determination of lead in naphtha and petroleum condensate

Sample	Lead added/ $\mu g\,L^{-1}$	Lead determined/ $\mu g\,L^{-1}$	Recovery/ %
Petroleum condensate 1	0	5.0 ± 0.3	–
	5.0	9.7 ± 0.3	94
Petroleum condensate 2	0	5.4 ± 0.2	–
	5.0	10.0 ± 0.4	90
Petroleum condensate 3	0	2.7 ± 0.4	–
	5.0	7.6 ± 0.2	98
Naphtha 1	0	<2.6	–
	5.0	5.2 ± 0.3	104
Naphtha 2	0	<2.6	–
	5.0	5.3 ± 0.1	106

processes, which are affected profoundly by trace amounts of metals such as lead. Since it is a heavier fraction of petroleum compared to naphtha, petroleum condensate may contain higher concentration of metals, requiring more careful quality control when such product replaces naphtha as raw material in the petrochemical industry [28].

The proposed method was applied for the determination of lead in three petroleum condensate and two naphtha samples. The concentrations found for the petroleum condensate varied of 2.7–5.7 $\mu g\,L^{-1}$, while the naphtha samples did not contain any detectable lead, as shown in Table 6. These results are actually according to the above expectations that petroleum condensate would exhibit higher lead concentrations, and hence has to be controlled more carefully.

Conclusion

The method proposed has limit of detection, precision and accuracy necessary for the determination of lead in naphtha and condensate samples. The use of the standard calibration technique with organic standard solutions makes the procedure quite simple, fast and suitable for routine purposes. It might be expected that other trace heavy metals could be determined in a similar way in these matrices. This paper reports the first method proposed for the determination of lead in petroleum condensate.

References

[1] Hardaway C, Sneddon J, Beck J N (2004) Determination of metals in crude oil by atomic Spectroscopy. Anal Lett 37: 2881

[2] Munoz R A A, Silva C S, Correia P R M, Oliveira P V, Angnes L (2005) Potentiometric stripping analysis for simultaneous determination of copper and lead in lubricating oils after total digestion in a focused microwave-assisted oven. Microchim Acta 149: 199

[3] Vale M G R, Damin I C F, Klassen A, Silva M M, Welz B, Silva A F, Lepri F G, Borges D L G, Heitmann U (2004) Method development for the determination of nickel in petroleum using line-source and high-resolution continuum-source graphite furnace atomic absorption spectrometry. Microchem J 77: 131

[4] Aucelio R Q, Doyle A, Pizzorno B S, Tristão M L B, Campos R C (2004) Electrothermal atomic absorption spectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless microemulsions. Microchem J 78: 21

[5] Rebouças M V, Ferreira S L C, Barros Neto B (2003) Arsenic determination in naphtha by electrothermal atomic absorption spectrometry after preconcentration using multiple injections. J Anal At Spectrom 18: 1267

[6] Amaro J A A, Ferreira S L C (2004) Application of factorial design and Doehlert matrix in the optimisation of instrumental parameters for direct determination of silicon in naphtha using graphite furnace atomic absorption spectrometry. J Anal At Spectrom 19: 246

[7] Xiang G Q, Jiang Z C, He M, Hu B (2006) Simultaneously direct determination trace elements and its distribution in ancient tooth samples by slurry sampling-electrothermal vaporization inductively coupled plasma mass spectrometry. Microchim Acta 154: 247

[8] Acar O (2005) Determination of lead, chromium, manganese and zinc in slurries of botanical and biological samples by electrothermal atomic absorption spectrometry using tungsten-containing chemical modifiers. Microchim Acta 151: 53

[9] Reyes M N M, Campos R C (2005) Graphite furnace atomic absorption spectrometric determination of Ni and Pb in diesel and gasoline samples stabilized as microemulsion using conventional and permanent modifiers. Spectrochim Acta Part B 60: 615

[10] Kowalewska Z, Bulska E, Hulanicki A (1999) Organic palladium and palladium–magnesium chemical modifiers in direct determination of lead in fractions from distillation of crude oil by electrothermal atomic absorption analysis. Spectrochim Acta Part B 54: 835

[11] Anselmi A, Tittarelli P, Katskov D A (2002) Determination of trace elements in automotive fuels by filter furnace atomic absorption spectrometry. Spectrochim Acta Part B 57: 403

[12] Nakamoto Y (2004) Rapid determination of lead in thermally cracked gasoline by graphite furnace AAS. Bunseki Kagaku 53: 13

[13] Campos R C, Santos H R, Grinberg P (2002) Determination of copper, iron, lead and nickel in gasoline by electrothermal atomic absorption spectrometry using three-component solutions. Spectrochim Acta Part B 57: 15

[14] Turunen M, Peraniemi S, Ahlgren S, Westerholm H (1995) Determination of trace-elements in heavy oil samples by graphite-furnace and cold vapor atomic-absorption spectrometry after acid digestion. Anal Chim Acta 311: 85

[15] Alswaidan H M (1996) The determination of lead, nickel and vanadium in Saudi Arabian crude oil by sequential injection analysis inductively-coupled plasma mass spectrometry. Talanta 43: 1313

[16] Alswaidan H M (1994) Microemulsion determination of lead and cadmium in Saudi-Arabian petroleum-products by inductively-coupled plasma-mass spectrometry (ICP-MS). Sci Total Environ 145: 157

[17] Ferreira S L C, dos Santos W N L, Quintella C M, Neto B B, Bosque-Sendra J M (2004) Doehlert matrix: a chemometric tool for analytical chemistry – review. Talanta 63: 1061

[18] Manzoori J L, Amjadi M (2003) Spectrofluorimetric determination of piroxicam in pharmaceutical preparations and spiked human serum using micellar media. Microchim Acta 143: 39

[19] Ferreira A C, Costa A C S, Korn M G A (2004) Preliminary evaluation of the cadmium concentration in seawater of the Salvador City, Brazil. Microchem J 78: 77

[20] dos Santos W L, dos Santos C M M, Costa J L O, Andrade H M, Ferreira S L C (2004) Multivariate optimization and validation studies in on-line pre-concentration system for lead determination in drinking water and saline waste from oil refinery. Microchem J 77: 123

[21] de Souza R M, Mathias B M, Scarminio I S, da Silveira C L P, Aucelio R Q (2006) Comparison between two sample emulsification procedures for the determination of Mo, Cr, V and Ti in diesel and fuel oil by ICPOES along with factorial design. Microchim Acta 153: 219

[22] Ferreira A C, Korn M D A, Ferreira S L C (2004) Multivariate optimization in preconcentration procedure for manganese determination in seawater samples by FAAS. Microchim Acta 146: 271

[23] Ferreira H S, Bezerra M D, Ferreira S L C (2006) A preconcentration procedure using cloud point extraction for the determination of uranium in natural water. Microchim Acta 154: 163

[24] Massart D L, Vandeginste B G M, Buydens L M C, de Jong S, Lewi P J, Smeyers-Verbeke J (1998) Handbook of Chemometrics and Qualimetrics. Part A. Elsevier, Amsterdam

[25] dos Santos W N L, Dias F S, Fernandes M S, Rebouças M V, Vale M G R, Welz B, Ferreira S L C (2005) Application of multivariate technique in method development for the direct determination of copper in petroleum condensate using graphite furnace atomic absorption spectrometry. J Anal At Spectrom 20: 127

[26] da Silva A F, Welz B, Curtius A J (2002) Noble metals as permanent chemical modifiers for the determination of mercury in environmental reference materials using solid sampling graphite furnace atomic absorption spectrometry and calibration against aqueous standards. Spectrochimica Acta Part B 57: 2031

[27] Statistica for Windows, StatSoft, Inc (1999) 2300 East 14th Street, Tulsa, OK 741014, USA

[28] Rebouças M V (2004) Determinação de arsênio em nafta e condensado de petróleo por espectrometria de absorção atômica com atomização eletrotérmica utilizando lantânio como modificador, PhD Thesis, Universidade Federal da Bahia, Brasil